ADVANCED RESEARCH PROJECTS AGENCY

Contract SD-88

Technical report No. ARPA-18

CALCULATIONS OF THE VIBRATIONAL SPECTRA OF DISORDERED SYSTEMS

I. VIBRATIONAL SPECTRUM OF A ONE-DIMENSIONAL CHAIN WITH RANDOMLY DISTRIBUTED IMPURITY SPRINGS

II. THE ELASTIC SPECTRA OF TWO-DIMENSIONAL DISORDERED LATTICES

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December 1965

Submitted to:

Advanced Research Projects Agency

The Department of Defense

Division of Engineering and Applied Physics

Harvard University

Cambridge, Massachusetts

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1. VIBRATIONAL SPECTRUM OF A ONE-DIMENSIONAL CHAIN WITH RANDOMLY DISTRIBUTED IMPURITY SPRINGS

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ABSTRACT

The frequency spectrum of a one-dimensional lattice containing randomly distributed impurity springs has been evaluated to first order in the concentration, q, of impurity springs. It is shown that, with some mathematical manipulation, the solution can be placed into correspondence with the solution of Langer for the analogous problem of isotopic impurities. The virtual crystal approximation which yields the correct elastic constants requires an effective spring constant, $\bar{\gamma}$, which is given, in terms of normal spring constant, γ, and the impurity spring constant, γ', by the relation $1/\bar{\gamma} = [(1-q)/\gamma] + q/\gamma'$.

I. INTRODUCTION

In recent years, considerable progress has been made in the calculation of the vibrational properties of solids with isotopic impurities [1]. For a variety of reasons, however, there has been less consideration of problems in which the interatomic force constants are varied.

Such problems appear, at first, to be unrelated to actual physical situations. In the disordering of two alloys of the beta-brass type, CuZn and CoFe, however, the constituents have almost identical atomic masses. The primary result of disordering appears to be a change of force constants. Since the change of the vibrational spectrum with order influences the equilibrium state of order, it will be necessary to understand these changes before a complete understanding of the order-disorder process is possible.

First steps in this direction have been made by Wojtowicz and Kirkwood [2] as well as Oguchi and Hiroike [3]. In both cases, however, there are approximations which considerably limit the applicability of the results. While it is highly likely that any solution of these problems will be approximate, there is reason to believe that more satisfactory approaches may be found. For that reason, we have turned our attention to the formal solutions of certain simplified problems. It is hoped that these solutions will lead to some insight that will, in turn, lead to better approximations. This first solution of a one-dimensional problem has been solved to develop useful mathematical procedure. Solutions of problems of higher dimensionality have been obtained. They will be presented when they are understood.

The problem which is treated here is that of a linear chain of atoms with the same mass and nearest neighbor interactions. Randomly positioned springs are replaced by springs which have a different force constant, and the spectral distribution function is calculated to first order in the concentration of the impurity springs. The mathematical techniques used are almost identical to those of Langer [4] who obtained an exact solution, to first order in the

concentration, for the spectral density function of a one-dimensional chain of identical atoms into which isotopic impurities are randomly placed. Indeed, we proceed by showing that the problem considered here can be placed in the same form as the problem which Langer considered, and then use his results.

The corresponding order-disorder problem is both simple and uninteresting. Consider a chain consisting of two distinct chemical species, A and B, of the same mass, which alternate in position in the ordered ground state. Let the ordering process and the vibrational spectrum be controlled by nearest neighbor interactions, such that the spring constant between A-B pairs is different from that between A-A and B-B nearest neighbor pairs. Let the force constants between A-A and B-B pairs be identical. Such a situation would be obtained from the polar model of Mott [5] or Harrison and Paskin [6] if their interactions were of sufficiently short range (which they are not) and if the repulsive interactions were all the same. The first configurational excited state of such a system is one in which there is an A-A or B-B pair somewhere along the chain, but perfect short range order elsewhere. That is, there is a simple antiphase boundary. The corresponding vibrational spectrum would be one for an isolated single impurity spring constant placed at random in the chain. The next excited state which maintained the composition would consist of two such antiphase boundaries. One would be between an A-A pair and another between a B-B pair, so that they would be separated from one another by more than a nearest neighbor distance. (This restriction can be lifted by the choice of suitably chosen grand

canonical ensemble.) It follows that the randomly placed impurity spring constant problem can be brought into close analogy with the one-dimensicnal order-disorder problem where the concentration of impurity springs is analogous to the decrease of the short range order parameter from unity.

It should be noted that the choice of randomly positioned impurity springs makes this solution applicable to the order-disorder problem, rather than the impurity problem. That is, one might be concerned with the effect of randomly distributed impurity atoms on the vibrational spectrum. The major feature of these impurities might very well be the changing of force constants, rather than the changing of the mass. To treat this problem, however, one would be obliged to consider randomly distributed pairs of impurity springs on the sides of the impurity atom, rather than randomly distributed single springs.

II. FORMULATION OF THE PROBLEM

The formulation of the problem presented here is similar to, and whenever possible and practical, identical to that presented by Langer [4]. We consider a very long chain in which every atom has the same mass. There are two types of force constants present in the chain, γ and γ'. The concentration of impurity force constants, γ', is q, where $q \ll 1$ The unperturbed chain has $q = 0$.

For a particular distribution of springs, γ and γ' along the chain, the equations of motion are

$$m \ddot{x}_l = \gamma_{l, l-1} (x_{l-1} - x_l) + \gamma_{l, l+1} (x_{l+1} - x_l) . \tag{1}$$

Here x_l is the displacement of the atom at the site l, and $\gamma_{l,\,l-1}$ is the force constant acting between atoms at site l and $l-1$. The equations of motion can be rewritten as

$$m \ddot{x}_l - \gamma \, (x_{l-1} - x_l) - \gamma \, (x_{l+1} - x_l)$$

$$= (\gamma_{l,\,l-1} - \gamma)\,(x_{l-1} - x_l) + (\gamma_{l,\,l+1} - \gamma)(x_{l+1} - x_l). \tag{2}$$

The transformation to the normal coordinates, Q_k, of the unperturbed lattice is

$$x_l = \frac{1}{(Nm)^{1/2}} \sum_{k=-N/2}^{N/2} Q_k \, \exp\left(\frac{2\pi \, ikl}{N} - i\omega t\right), \tag{3}$$

where N is the number of atoms in the chain. Substitution of Eq. (3) into Eq. (2) yields

$$(\omega_k^2 - \omega^2)\, Q_k = - \sum_{k'} \Phi_{k,\,k'} \, Q_{k'}, \tag{4}$$

where

$$\omega_k = \omega_m \, \left| \sin\left(\pi k/N\right) \right|, \qquad \omega_m = (4\gamma/m)^{1/2} \tag{5}$$

and

$$\Phi_{k,\,k'} = \frac{(-2i)\,\sin\left(\pi k'/N\right)}{Nm} \sum_l \exp\left[2\pi \, i \, (k'-k)l/N\right]$$

$$\times \quad \left[(\gamma_{l,\,l+1} - \gamma)\exp\left(\pi \, ik'/N\right) - (\gamma_{l,\,l-1} - \gamma)\exp\left(-\pi \, ik'/N\right)\right]. \tag{6}$$

Equation (4) is identical in form to Langer's Eq. (4). The entire difference between the two problems is contained in the explicit form of the $\Phi_{k, k'}$, as expressed in Eq. (6).

For a particular configuration of springs, we can write

$$[D^{-1}(\omega^2)]_{k, k'} = (\omega_k^2 - \omega^2)\, \delta_{k, k'} + \Phi_{k, k'} \tag{7}$$

such that Eq. (4) becomes

$$\sum_{k'} (D^{-1})_{k, k'}\, Q_{k'} = 0 \ . \tag{8}$$

Following Langer, the spectral distribution function for this configuration, defined by

$$g(\omega) = \lim_{N \to \infty} \frac{2\omega}{N} \sum_{n} \delta(\Omega_n^2 - \omega^2) \ , \tag{9}$$

where the Ω_n are the exact eigenfrequencies for the particular configuration of springs, is given by

$$g(\omega) = \frac{2\omega}{\pi} \lim_{\substack{N \to \infty \\ \epsilon \to 0}} \frac{1}{N} \operatorname{Im} \operatorname{Tr} D(\omega^2 + i\epsilon) \ . \tag{10}$$

To obtain the spectral distribution function for the random distribution of springs $\bar{g}(\omega)$, we must average over all configurations which are consistent with a fixed value of q. As shown by Langer, it is sufficient to take the configuration average, $\bar{D}(\omega^2 + i\epsilon)$, of $D(\omega^2 + i\epsilon)$. $\bar{D}(\omega^2 + i\epsilon)$ is diagonal in k , so that

$$\bar{g}(\omega) = \frac{2\omega}{\pi} \lim_{\substack{N \to \infty \\ \epsilon \to 0}} \frac{1}{N} \operatorname{Im} \sum_k \bar{D}_k (\omega^2 + i\epsilon).$$ (11)

III. CONFIGURATION AVERAGE

Following Langer, we obtain from Eq. (7) for a particular configuration,

$$D_{k, k'}(\omega^2) = \frac{\delta_{k, k'}}{\omega_k^2 - \omega^2} - \frac{1}{\omega_k^2 - \omega^2} \sum_{k''} \Phi_{k, k''} D_{k'', k'}(\omega^2)$$ (12)

which may be iterated to yield

$$D_{k, k'}(\omega^2) = \frac{1}{\omega_k^2 - \omega^2} \left[\delta_{k, k'} - \frac{\Phi_{k, k'}}{\omega_k^2 - \omega^2} + \sum_{k_1} \frac{\Phi_{k, k_1} \Phi_{k_1, k'}}{(\omega_{k_1}^2 - \omega^2)(\omega_{k'}^2 - \omega^2)} \right.$$
$$\left. + \ldots \ldots \right].$$ (13)

The average over configurations is performed at this point. Since the ω_k's are properties of the unperturbed lattice, it is only necessary to obtain configurational averages of the products $\Phi_{k, k_1} \Phi_{k_1, k_2} \cdots \Phi_{k_n, k'}$. We proceed to obtain these averages. The first, $< \Phi_{k, k'} >$ may be obtained in the same manner as Langer obtained his Eq. (19). We get

$$< \Phi_{k, k'} > = \frac{(-2i)\sin(\pi k'/N)}{Nm} < \sum_{\ell} \exp[2\pi i (k'-k) \ell/N]$$

$$\times \quad [(\gamma_{\ell, \ell+1} - \gamma) \exp(i\pi k'/N) - (\gamma_{\ell, \ell-1} - \gamma) \exp(-i\pi k'/N)] > .$$ (14)

This expression is evaluated by keeping l fixed while summing over configurations. We get zero contribution from any configuration in which $\gamma_{l,\,l+1}$ or $\gamma_{l,\,l-1} = \gamma$. Since $\gamma_{l,\,l+1} = \gamma'$ with frequency q, one obtains

$$< \gamma_{l,\,l+1} - \gamma> \; = \; < \gamma_{l,\,l-1} - \gamma> \; = \; q\,(\gamma' - \gamma) \,, \tag{15}$$

and

$$< \Phi_{k,\,k'} > \; = \; \frac{4 \sin^2(\pi k'/N)}{Nm} \; q\,(\gamma' - \gamma) \sum_{l} \exp\left[2\pi i l(k'-k)/N\right]$$

$$= \; q\,\omega_{k'}^2 \lambda \; \delta_{k,\,k'} \,, \tag{16}$$

where

$$\lambda \; = \; (\gamma'/\gamma) - 1 \,. \tag{17}$$

Next consider the second-order term,

$$< \Phi_{k,\,k_1} \Phi_{k_1,\,k'} > \; = \; (-4/N^2 m^2) \sin(\pi k_1/N) \sin(\pi k'/N)$$

$$\times \; < \sum_{l_1,\,l_2} \{ \exp 2\pi i (k_1 - k) l_1/N \; \exp 2\pi i (k' - k_1) l_2/N \tag{18}$$

$$\times \; [(\gamma_{l_1,\,l_1+1} - \gamma) \exp(\pi i k_1/N) \cdot (\gamma_{l_1,\,l_1-1} - \gamma) \exp(-\pi i k_1/N)]$$

$$\times \; [(\gamma_{l_2,\,l_2+1} - \gamma) \exp(\pi i k'/N) - (\gamma_{l_2,\,l_2-1} - \gamma) \exp(-\pi i k'/N)] \} > \,.$$

Terms which are first order in q appear in the configuration average of the four terms represented by the product of the square brackets whenever the two springs of one of the four terms are identical. That is, when $l_2 = l_1$,

$l_2 = l_1 - 1$, or $l_2 = l_1 + 1$. This complication distinguishes the problem considered here from that of Langer, in which only the terms $l_1 = l_2$ contribute to first order in q. This extra complication forces us to use a slightly different approach in the evaluation of the general product of the Φ's. For the second-order term, however, it is easy to sum the appropriate terms.

For terms with $l_1 = l_2$, we obtain

$$(-4/Nm^2) \sin(\pi k_1/N) \sin(\pi k'/N) \, \delta_{k,\,k'} \, q(\gamma'-\gamma)^2$$

$$x \; [\exp \pi i (k_1+k')/N + \exp - \pi i (k_1+k')/N] . \tag{19}$$

Terms with $l_2 = l_1-1$ yield

$$(4/Nm^2) \sin(\pi k_1/N) \sin(\pi k'/N) \, \delta_{k,\,k'} \, q(\gamma'-\gamma)^2 \exp[\pi i(k_1-k')/N] , \tag{20}$$

while terms with $l_2 = l_1+1$ yield

$$(4/Nm^2) \sin(\pi k_1/N) \sin(\pi k'/N) \, \delta_{k,\,k'} \, q(\gamma'-\gamma)^2 \exp[-\pi i(k_1-k')/N]. \tag{21}$$

Summing the contributions from (19), (20), and (21), we obtain

$$< \Phi_{k,\,k_1} \Phi_{k_1,\,k'} > = (\omega_{k_1}^2 \omega_{k'}^2/N) \, q\lambda^2 \, \delta_{k,\,k'} + O(q^2) . \tag{22}$$

It should be noted that although the intermediate steps are different, the result is identical to Langer's Eq. (22).

We now proceed to evaluate the configuration average of the general product,

$$< \Phi_{k, k_1} \Phi_{k_1, k_2} \cdots \Phi_{k_{n-1}, k_n} >$$

$$= \frac{(-2i)^n}{N^n m^n} \sin\left(\frac{\pi k_1}{N}\right) \sin\left(\frac{\pi k_2}{N}\right) \cdots \sin\left(\frac{\pi k_{n-1}}{N}\right) \sin\left(\frac{\pi k_n}{N}\right)$$

$$x \quad < \sum_{\ell_1} \sum_{\ell_2} \cdots \sum_{\ell_n} \exp \frac{2\pi i}{N} [(k_1-k)\ell_1 + (k_2-k_1)\ell_2 + \cdots + (k_n - k_{n-1})\ell_n]$$

$$x \quad [(\gamma_{\ell_1, \ell_1+1} - \gamma) \exp(\pi i k_1/N) - (\gamma_{\ell_1, \ell_1-1} - \gamma) \exp(-\pi i k_1/N)]$$

$$x \quad [(\gamma_{\ell_2, \ell_2+1} - \gamma) \exp(\pi i k_2/N) - (\gamma_{\ell_2, \ell_2-1} - \gamma) \exp(-\pi i k_2/N)]$$

$$x \quad \cdots \cdots \cdots$$

$$x \quad [(\gamma_{\ell_n, \ell_{n+1}} - \gamma) \exp(\pi i k_n/N) - (\gamma_{\ell_n, \ell_{n-1}} - \gamma) \exp(-\pi i k_n/N)] > , \tag{23}$$

where $k_n = k'$. Equation (23) can be written in the form

$$< \Phi_{k, k_1} \cdots \Phi_{k_{n-1}, k_n} >$$

$$= \frac{(-2i)^n}{N^n m^n} \prod_{j=1}^{n} \sin\left(\frac{\pi k_j}{N}\right)$$

$$x < \sum_{\ell_1 \cdots \ell_n} \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_n = \pm 1} \{ \exp \frac{2\pi i}{N} [(k_1-k)\ell_1 + \cdots + (k_n - k_{n-1})\ell_n] \tag{24}$$

$$x \quad \prod_{j=1}^{n} [\sigma_j (\gamma_{\ell_j, \ell_j + \sigma_j} - \gamma) \exp(\pi i \sigma_j k_j/N)] \} > .$$

Let us fix our attention on a particular l_1. For $\sigma_1 = +1$, Eq. (24) will yield terms of order q only if, for all values of $s = 2, 3, \ldots, n$ $l_s = l_1$ and $\sigma_s = +1$, or $l_s = l_1 + 1$ and $\sigma_s = -1$. Similarly, for $\sigma_1 = -1$, terms of order q will be obtained only if $l_s = l_1$ and $\sigma_s = -1$ or $l_s = l_1 - 1$ and $\sigma_s = +1$. These restrictions are summarized by the condition that

$$l_s = l_1 + \frac{1}{2} (\sigma_1 - \sigma_s) . \tag{25}$$

Thus, we obtain all the terms of order q in Eq. (24) by substituting Eq. (25) into it, dropping the summations over all l_j but $l_j = l_1$, but retaining the summations over the σ_j. The result is

$$< \Phi_{k, k_1} \cdots \Phi_{k_{n-1}, k_n} >$$

$$= \frac{(-2i)^n}{N^n m^n} q (\gamma' - \gamma)^n \left[\prod_{j=1}^{n} \sin (\frac{\pi k_j}{N}) \right] \times \sum_{l_1} \exp [\frac{2\pi i}{N} (k_n - k) l_1]$$

$$\times \sum_{\sigma_1 = \pm 1} \cdots \sum_{\sigma_n = \pm 1} \sigma_1 \exp (\frac{i\pi \sigma_1 k_1}{N}) \prod_{j=2}^{n} \sigma_j \exp [\frac{\pi i}{N} (k_j - k_{j-1})(\sigma_1 - \sigma_j) + \sigma_j k_j] . \tag{26}$$

The summation over l_1 in Eq. (26) can be performed immediately. This leaves the summations over the σ variables. The coefficients of k_s in the exponents which remain are

$$\{i\pi [\sigma_1 - (\sigma_1 - \sigma_2)]/N\} = (i\pi \sigma_2/N) \qquad \text{for} \qquad s = 1 ,$$

$$\{i\pi [(\sigma_1 - \sigma_s) + \sigma_s - (\sigma_1 - \sigma_{s+1})]\} = (i\pi \sigma_{s+1}/N) \quad \text{for} \quad s = 2, \ldots, n-1, \tag{27}$$

$$\{i\pi [(\sigma_1 - \sigma_n) + \sigma_n]/N\} = (i\pi \sigma_1/N) \qquad \text{for} \quad s = n .$$

Therefore, Eq. (26) can be rewritten as

$$
< \Phi_{k, k_1} \cdots \Phi_{k_{n-1}, k_n} >
$$

$$
= \frac{(-2i)^n}{N^{n-1} m^n} \left[\prod_{j=1}^{n} \sin \left(\frac{\pi k_j}{N} \right) \right] \times \ \delta_{k, k_n} \ q \ (\gamma' - \gamma)^n
$$

$$
\times \sum_{\sigma_1 \cdots \sigma_n} \left(\prod_{j=1}^{n} \sigma_j \right) \exp \left[\frac{\pi i}{N} (\sigma_2 k_1 + \sigma_3 k_2 + \ldots + \sigma_n k_{n-1} + \sigma_1 k_n) \right] .
$$

(28)

Since the σ_j are equivalent variables of summation, Eq. (28) can be rewritten as

$$
< \Phi_{k, k_1} \cdots \Phi_{k_{n-1}, k_n} >
$$

$$
= \frac{(-2i)^n}{N^{n-1} m^n} \ q \ (\gamma' - \gamma)^n \left(\prod_{j=1}^{n} \sin \frac{\pi k_j}{N} \right) \sum_{\sigma_1 \cdots \sigma_n} \prod_{j=1}^{n} \sigma_j \exp \left(\frac{\pi i \ \sigma_j k_j}{N} \right) .
$$

(29)

In this form, the sums can be performed readily. Using Eq. (5), the average becomes

$$
< \Phi_{k, k_1} \cdots \Phi_{k_{n-1}, k_n} > = \delta_{k, k_n} q \lambda^n \ \omega_k^2 \ \omega_{k_1}^2 \cdots \omega_{k_{n-1}}^2 / N^{n-1} .
$$

(30)

Equation (30) is completely equivalent to the term which is linear in q in Langer's Eq. (25).

IV. THE VIBRATIONAL SPECTRUM

Because of the equivalence presented above, it is possible to use
Langer's results directly. He finds vibrational modes associated with each
value of k, and with frequency given by

$$\omega = \omega_k + \Delta_k - i\Gamma_k \quad . \tag{31}$$

Here,

$$\Delta_k = \frac{\omega_k}{2} \frac{q\kappa(\omega_m^2 - \omega_k^2)}{\omega_m^2 - \omega_k^2(1-\kappa^2)} \tag{32}$$

and

$$\Gamma_k = \frac{\omega_k}{2} \frac{q\kappa^2 \omega_k (\omega_m^2 - \omega_k^2)^{1/2}}{\omega_m^2 - \omega_k^2(1-\kappa^2)} \quad , \tag{33}$$

where

$$\kappa = \lambda/(1+\lambda) = 1 - (\gamma/\gamma') \quad . \tag{34}$$

In these expressions, Γ_k is a measure of the width associated with each
phonon of wave vector k due to the lattice disorder.

In addition, the density of states is given by

$$\bar{g}(\omega) = \frac{2}{\pi} \ \mathrm{Re} \left[\omega_m^2 - \omega^2 + \frac{\omega_m^2 q\kappa(\omega_m^2 - \omega^2)^{1/2}}{(\omega_m^2 - \omega^2)^{1/2} + i\kappa\omega} \right]^{-1/2} \quad . \tag{35}$$

Since Langer has discussed his results extensively and carefully,
we shall only draw attention to certain aspects of the results which were not,
apparently, of primary interest to him, or are unique to the problem considered

It should be noted, however, that it is $1/\gamma$ and $1/\gamma'$ in this work

which correspond to Langer's M and M', respectively. This correspondence

becomes obvious when the different definitions of λ are examined.

In the long wavelength limit, and with $\gamma' \approx \gamma$

$$\omega^2 \approx 4 \sin \left(\frac{\pi k}{N}\right) / M[(1-q)\frac{1}{\gamma} + \frac{q}{\gamma'}] . \tag{36}$$

Thus, in the elastic limit, an average spring constant can be defined by

$$\frac{1}{\overline{\gamma}} = \frac{(1-q)}{\gamma} + \frac{q}{\gamma'} . \tag{37}$$

The frequency spectrum is, in this limit, identical to that which would

be obtained if all the springs were replaced by the correctly averaged spring.

It is important to note, however, that this correct averaging, to obtain

a virtual crystal approximation, is of $1/\gamma$, rather than γ itself.

While this result might be expected, its application, as an approximation

to a two or three dimensional system, is highly suspect. The obvious reason

for this is as follows. When the linear chain is placed in tension, the atoms

adjacent to the impurity springs are constrained to move along the line of

tension. The analogous situation in three dimensions is one in which tension

is applied in a manner which corresponds to the limit of a pure longitudinal

mode of the unperturbed lattice. When the impurity springs are introduced,

however, equilibrium may be reached by displacements which have components

normal to the direction of the tension. In this case Eq. (37) is not valid.

It is also of some interest to examine the form of Γ_k, as given in Eq. (33). It is easily seen that $\Gamma_k = 0$ for $\omega_k = 0$ or $\omega_k = \omega_m$. Since Γ_k is positive, it must have a maximum somewhere in between these two points. That maximum occurs for

$$\omega_k^2 = \omega_m^2 \left[\frac{3 - (1 + 8\kappa^2)^{1/2}}{2(1-\kappa^2)} \right] \tag{38}$$

for all possible values of κ^2. The functional form of Γ_k is shown in Fig. 1. The maximum is quite evident. In the paragraphs which follow, an attempt is made to explain this behavior.

The mathematical origin of these widths is discussed by Langer. Each member of the ensemble is not periodic, and k does not label an eigenvector. Thus, a measurement which fixes k will yield a spread in frequencies. Although k becomes, in a certain sense, a good label for the ensemble average, the spread in frequencies must remain. Mathematically, we see the spread in the form of the average spectral distribution function,

$$\bar{g}(\omega) = \frac{2\omega}{\pi} \lim_{\substack{N\to\infty \\ \epsilon\to 0}} \frac{1}{N} \operatorname{Im} \sum_k D_k(\omega^2 + i\epsilon) . \tag{39}$$

For the unperturbed chain,

$$D_k(\omega^2 + i\epsilon) = 1/(\omega_k^2 - \omega^2 - i\epsilon) . \tag{40}$$

The poles of $D_k(\omega^2)$ occur at the eigenvalues associated with k. Langer's results may be paraphrased as follows. For the perturbed problem, there are a number of frequencies, denoted $\omega_{k,i}$, which are positions of the poles of each $D_k(\omega^2 + i\epsilon)$. These poles lie at the solutions of

$$\omega_k^2 - \omega_{k,i}^2 + G_k(\omega_{k,i}^2) = 0 \tag{41}$$

where, from Langer's work,

$$G_k(\omega^2) = \frac{q \kappa \omega_k^2}{1 + \frac{\kappa \omega^2}{N} \sum_{k'} \frac{1}{\omega_{k'}^2 - \omega^2}} \tag{42}$$

to first order in q .

The contribution to $\bar{g}(\omega)$ from any one of the frequencies associated with k is proportional to the residue at the corresponding pole of $D_k(\omega^2)$, which is

$$\operatorname*{Res}_{\omega=\omega_{k,i}} \{D_k(\omega^2)\} = \left[-2\omega_{k,i} + (\partial/\partial\omega) \, G_k(\omega^2)\big|_{\omega=\omega_{k,i}}\right]^{-1} \, . \tag{43}$$

As indicated in Fig. 2, this residue is largest for $\omega_{k,i}$ in the vicinity of ω_k and diminishes rapidly on either side of this point as $(\partial G/\partial \omega)\big|_{\omega=\omega_{k,i}}$ becomes large.

With these results of Langer, the mathematical origin of the form of Fig. 1 is readily visualized. For each k , Γ_k is proportional to the range in ω over which the $\omega_{k,i}$ have appreciable residues. Let n_k be the number of modes for which the residues associated with the $\omega_{k,i}$ are appreciable, and ρ_k be the density of modes of the unperturbed system. Then

$$\Gamma_k \propto n_k/\rho_k \propto n_k (\omega_m^2 - \omega_k^2)^{1/2} \, . \tag{44}$$

Thus, it is the singularity in the density of states which causes the vanishing of Γ_k for $\omega_k = \omega_m$. That is, although n_k may be large for $k = k_{max}$, the infinite density of states causes the total energy spread to be very small.

It is evident that $\Gamma_k = 0$ for $k = 0$. The form of the increase of Γ_k with increasing k, up to the maximum is shown more explicitly, however, by an examination of Figs. 2 and 3. In these figures, $G_k(\omega^2)$ and $(\omega^2 - \omega_k^2)$ are plotted versus ω^2 for the cases $\omega_k^2 \ll \omega_m^2$ and $\omega_k^2 \approx \omega_m^2$. The intersections of $G_k(\omega^2)$ with $(\omega^2 - \omega_k^2)$ occur at the values of ω^2 equal to the $\omega_{k,i}^2$. The residue associated with these $\omega_{k,i}^2$ is appreciable, however, only at those values of $\omega_{k,i}^2$, such that $\partial G/\partial \omega$ is small. In Fig. 2, only the central $\omega_{k,i}$ satisfies this condition, while in Fig. 3, there are a number of terms for which the residue is appreciable. Thus, in the form of Eq. (44), the maximum in Γ_k may be pictured as a competition between the slowly increasing n_k and ρ_k which increases more slowly for small k, but increases rapidly near k_{max}.

V. ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1   The functional form of Γ_k for the case of

$\kappa = 2/3, \; q = 1/10.$

Fig. 2 $G_k(\omega^2)$ and $(\omega^2 - \omega_k^2)$ versus ω^2 for $\omega_k^2 << \omega_m^2$.

Fig. 3 $G_k(\omega^2)$ and $(\omega^2 - \omega_k^2)$ versus ω^2 for $\omega_k^2 \approx \omega_m^2$.
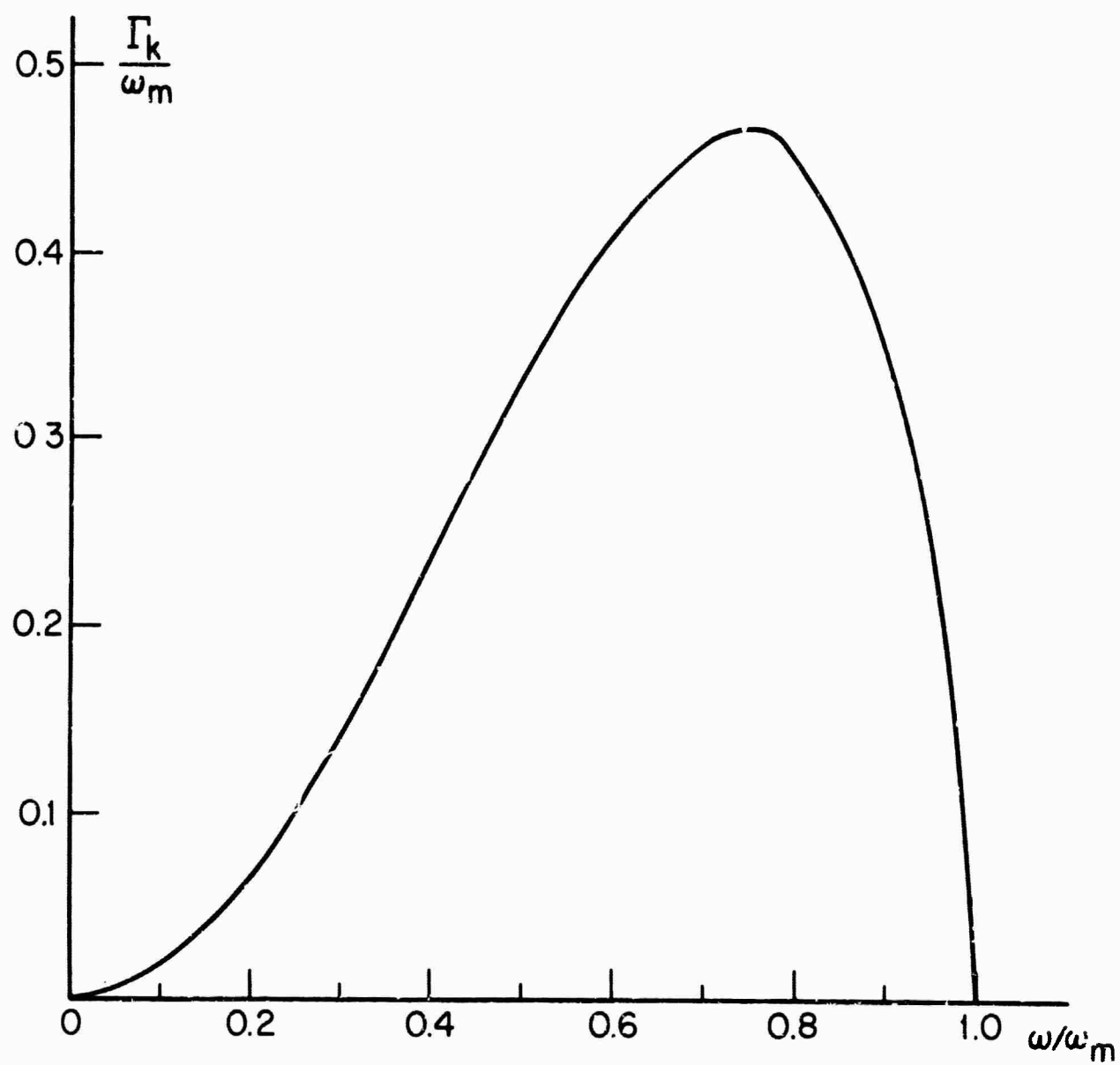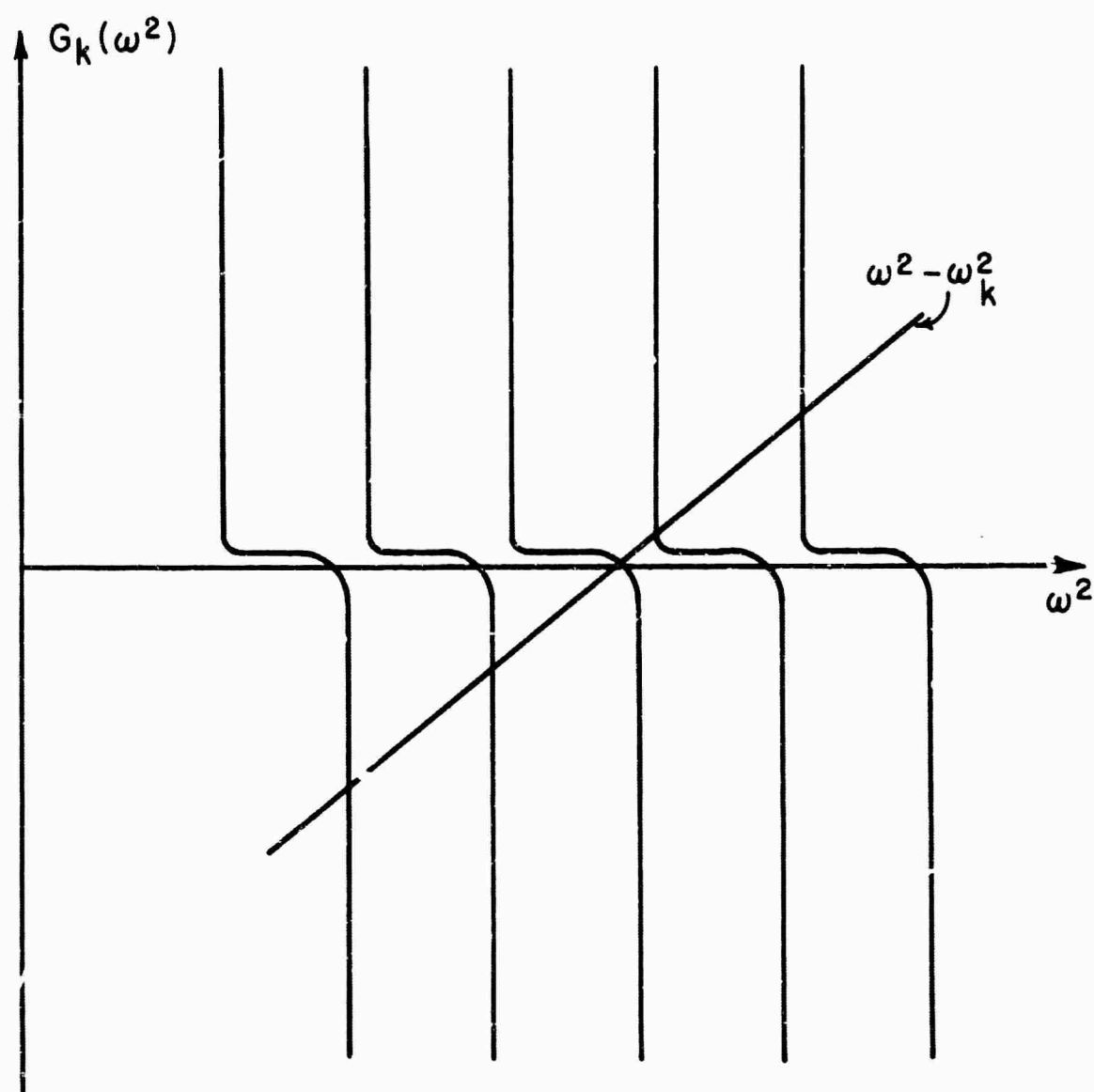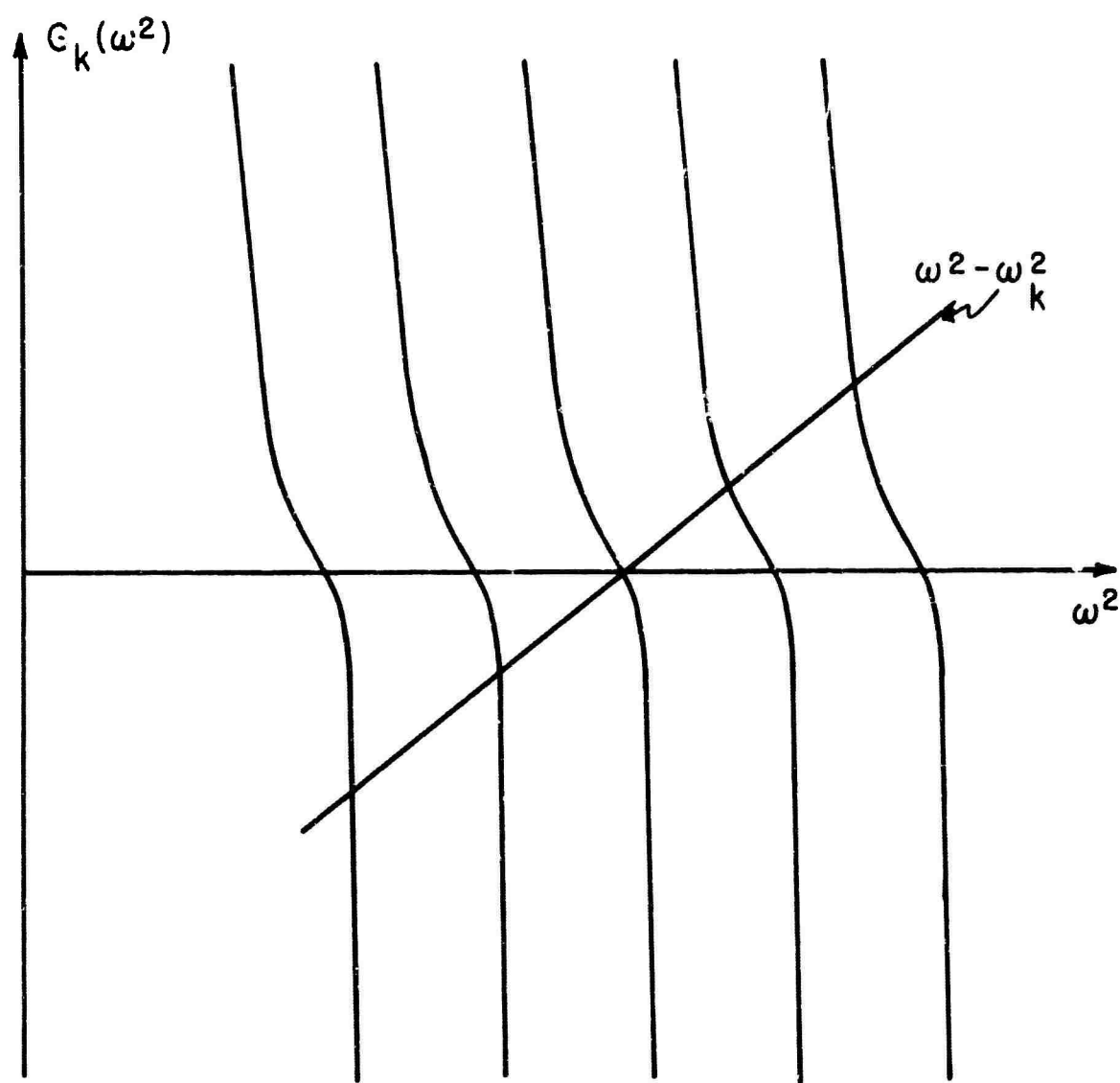
FIGURE 1

FIGURE 2

FIGURE 3

2. THE ELASTIC SPECTRA CF
TWO-DIMENSIONAL DISORDERED LATTICES

by

Hin-Chiu Poon and Arthur Bienenstock

ABSTRACT

The elastic vibrational spectra of perturbed square lattice systems with nearest-neighbor central and noncentral interactions have been derived. The unperturbed system consists of masses, m, on the lattice points and interacting with force constants, α, which determines the resistance to compression, and β, which determines the resistance to shear along the direction (10). In one case, the perturbations are Nq randomly positioned isotopic impurities of mass m', where N is the number of lattice sites. It is shown that the elastic spectrum for this, and all other isotopic impurity systems, is completely determined by the average mass, $\overline{m} = (1-q)m + qm'$. In the other case, corresponding to certain order-disorder situations, the constants describing the interactions between $2Nq$ randomly positioned pairs of nearest neighbors are replaced by α' and β'. To first order in q, the resulting elastic modes are then completely determined by an average α, $\overline{\alpha}$, where

$$\overline{\alpha} = \alpha \left[1 + \frac{q\,(\alpha'-\alpha)}{\alpha + (\alpha'-\alpha)(2/\pi)\tan^{-1}(\alpha/\beta)^{1/2}} \right]$$

and $\overline{\beta}$ which is obtained from the previous expression via the interchange of α and β. The appearance of β in the expression for $\overline{\alpha}$ implies that the virtual crystal approximation fails. It is shown, however, that two different

forms of the virtual crystal approximation place bounds on the $\bar{\alpha}$ and $\bar{\beta}$, in accordance with a general theory of Paul. A physical interpretation of the results is also presented.

I. INTRODUCTION

In a recent paper [1] (denoted, hereafter, as P-B) the authors obtained an expression for the vibrational frequency spectrum of a one-dimensional chain of atoms with the same mass and nearest-neighbor interactions. Randomly positioned springs were replaced by springs which had a different force constant, and the spectral distribution function was calculated to first order in the concentration of the impurity springs. The mathematical techniques used were a modification of those used by Langer [2] to solve the identical problem for the same unperturbed system in which the impurities were atoms with a different mass. While the motivation for the previous paper was an attempt to obtain more information about the effect of disordering on the vibrational spectrum of binary alloys such as CuZn and CoFe, in which the masses of the two constituents are almost identical, the one-dimensional nature of the problem limited the value of the solution. Nevertheless, the mathematical techniques developed are quite helpful, and will be used here.

In this paper, two related problems are treated. In both cases, the unperturbed lattice is a square lattice array of atoms with same mass, and with nearest-neighbor central and noncentral forces. In one case, the two force constants describing the interaction between randomly positioned nearest-neighbor pairs of atoms are replaced by a different pair of force constants. In the other, randomly positioned atoms are replaced by atoms of a different mass.

For convenience, we call the problems the impurity spring and impurity mass problems. In both cases, the elastic constants are obtained as a function of concentration, q, to first order in q.

The most striking feature of the results are that while the virtual crystal approximation is found to be valid for the impurity mass problem, it is valid only for special cases in the impurity spring problem. The explanation and implications of this result are discussed.

II. THE UNPERTURBED CASE

In the unperturbed case, we are considering the vibrational spectrum of a square lattice array of atoms of mass m. In order to maintain both stability and only nearest-neighbor interactions, these interactions must be noncentral. We label the atom at the origin by $(0,0)$ and its four nearest neighbors by $(1,0)$, $(0,1)$, $(\bar{1},0)$, and $(0,\bar{1})$. The equations of motion of the l-th atom are then

$$m \ddot{x}_{l,\alpha} + \sum_{l',\alpha'} C_{\alpha\alpha'} (l, l') \, x_{l',\alpha'} = 0 \,. \tag{1}$$

Here, the l' summation runs over the atom l and its four nearest neighbors, and the α' summation runs over the two orthogonal coordinates.

The force constant matrices have the forms

$$C(1,0) = C(\bar{1},0) = -\begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \,,$$

$$C(0,1) = C(0,\bar{1}) = -\begin{pmatrix} \beta & 0 \\ 0 & \alpha \end{pmatrix} \,,$$

$$C(0,0) = 2(\alpha+\beta)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{2}$$

For central force interactions, $\beta = 0$ and the lattice shows zero frequency shear modes for propagation along certain principal directions.

Expressing the displacements in terms of normal modes,

$$x_{\ell,\gamma} = \sum_{\underline{k},j} Q_{j,\gamma}(\underline{k}) \exp i(\underline{k} \cdot \underline{R}_\ell - \omega_{j,\underline{k}} t) , \tag{3}$$

where j (= 1 or 2) labels the two orthogonally polarized modes, and γ labels a displacement component, we obtain the normal mode solutions,

$$\omega_{1,\underline{k}}^2 = \frac{4}{m} [\alpha \sin^2 \frac{k_x a}{2} + \beta \sin^2 \frac{k_y a}{2}] ,$$

$$\omega_{2,\underline{k}}^2 = \frac{4}{m} [\beta \sin^2 \frac{k_x a}{2} + \alpha \sin^2 \frac{k_y a}{2}] , \tag{4}$$

with eigenvectors

$$Q_1(\underline{k}) = \binom{1}{0} , \qquad Q_2(\underline{k}) = \binom{0}{1} . \tag{5}$$

Equation (5) implies that for any propagation vector $\underline{k}$, the two normal modes, 1 and 2, have polarization vectors along $\hat{x}$ and $\hat{y}$, respectively. Thus, one of the two labels, j and γ, of $Q_{j,\gamma}$ in Eq. (3) is redundant, and will not be used hereafter.

III. THE IMPURITY SPRING PROBLEM

A. Formulation

In this problem, the force constants, α and β, associated with $2N$ randomly positioned pairs of atoms, are replaced by force constants α' and β'. To simplify the equations of motion, the four nearest neighbors of an atom which are separated from it by vectors $(1, 0)$, $(\bar{1}, 0)$, $(0, 1)$, and $(0, \bar{1})$ are denoted by $(\ell+1)$, $(\ell+2)$, $(\ell+3)$, and $(\ell+4)$, respectively. The equations of motion can then be written in the general form

$$
-\omega^2 m \begin{pmatrix} x_{\ell,1} \\ x_{\ell,2} \end{pmatrix} + \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \begin{pmatrix} 2x_{\ell,1} - x_{\ell+1,1} - x_{\ell+2,1} \\ 2x_{\ell,2} - x_{\ell+1,2} - x_{\ell+2,2} \end{pmatrix}
$$

$$
+ \begin{pmatrix} \beta & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} 2x_{\ell,1} - x_{\ell+3,1} - x_{\ell+4,1} \\ 2x_{\ell,2} - x_{\ell+3,2} - x_{\ell+4,2} \end{pmatrix}
$$

$$
= \begin{pmatrix} \alpha - \alpha_{\ell,\ell+1} & 0 \\ 0 & \beta - \beta_{\ell,\ell+1} \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+1,1} \\ x_{\ell,2} - x_{\ell+1,2} \end{pmatrix}
$$

$$
+ \begin{pmatrix} \alpha - \alpha_{\ell,\ell+2} & 0 \\ 0 & \beta - \beta_{\ell,\ell+2} \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+2,1} \\ x_{\ell,2} - x_{\ell+2,2} \end{pmatrix}
$$

$$
+ \begin{pmatrix} \beta - \beta_{\ell,\ell+3} & 0 \\ 0 & \alpha - \alpha_{\ell,\ell+3} \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+3,1} \\ x_{\ell,2} - x_{\ell+3,2} \end{pmatrix}
$$

$$
+ \begin{pmatrix} \beta - \beta_{\ell,\ell+4} & 0 \\ 0 & \alpha - \alpha_{\ell,\ell+4} \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+4,1} \\ x_{\ell,2} - x_{\ell+4,2} \end{pmatrix}
\tag{6}
$$

Equation (6) can be rewritten in terms of the normal coordinates of the transformation

$$x_{l,\gamma} = \sum_{\underline{k}} Q_\gamma(\underline{k}) \exp i\underline{k} \cdot \underline{R}_l \quad . \tag{7}$$

Since all the force constant matrices are diagonal, the x and y components of the displacement are independent. Thus, equations of motion can be written simply for each direction, using Eqs. (6) and (7). In addition, the two directions aɪ indistinguishable. Thus, it is sufficient to study one direction of polarization over a complete quadrant of the propagation plane. For the x-components of the displacements, we have

$$-\omega^2 m x_{l,1} + \alpha (2x_{l,1} - x_{l+1,1} - x_{l+2,1}) + \beta (2x_{l,1} - x_{l+3,1} - x_{l+4,1})$$

$$= (\alpha - \alpha_{l,l+1})(x_{l,1} - x_{l+1,1}) + (\alpha - \alpha_{l,l+2})(x_{l,1} - x_{l+2,1})$$

$$+ (\beta - \beta_{l,l+3})(x_{l,1} - x_{l+3,1}) + (\beta - \beta_{l,l+4})(x_{l,1} - x_{l+4,1}) \quad . \tag{8}$$

By substituting Eq. (7) into Eq. (8), and using Eq. (4) to simplify the resulting expression, one obtains

$$-m\omega^2 \sum_{\underline{k}} Q_1(\underline{k}) \exp i\underline{k} \cdot \underline{R}_l + m \sum_{\underline{k}} \omega^2_{1,\underline{k}} Q_1(\underline{k}) \exp i\underline{k} \cdot \underline{R}_l$$

$$= (\alpha - \alpha_{l,l+1}) \sum_{\underline{k}} Q_1(\underline{k}) (1 - \exp i k_x a) \exp i\underline{k} \cdot \underline{R}_l$$

$$+ (\alpha - \alpha_{l,l+2}) \sum_{\underline{k}} Q_1(\underline{k})(1 - \exp -i k_x a) \exp i\underline{k} \cdot \underline{R}_l$$

$$+ (\beta - \beta_{l,l+3}) \sum_{\underline{k}} Q_1(\underline{k})(1 - \exp i k_y a) \exp i\underline{k} \cdot \underline{R}_l$$

$$+ (\beta - \beta_{l,l+4}) \sum_{\underline{k}} Q_1(\underline{k})(1 - \exp -i k_y a) \exp i\underline{k} \cdot \underline{R}_l \quad . \tag{9}$$

After multiplying both sides of Eq. (9) by $\exp-i\underline{k}'\cdot\underline{R}_\ell$ and summing over ℓ, one obtains

$$m N (\omega_{1,k'}^2 - \omega^2) Q_1(\underline{k}')$$

$$= \sum_{\ell,k} Q_1(\underline{k}) \exp i(\underline{k}-\underline{k}')\cdot\underline{R}_\ell$$

$$\times [(\alpha-\alpha_{\ell,\ell+1})(1-\exp i k_x a) + (\alpha-\alpha_{\ell,\ell+2})(1-\exp-i k_x a)$$

$$+ (\beta-\beta_{\ell,\ell+3})(1-\exp i k_y a) + (\beta-\beta_{\ell,\ell+4})(1-\exp-i k_y a)] . \tag{10}$$

After interchanging $\underline{k}$ and $\underline{k}'$ and performing some trivial mathematical manipulations, Eq. (10) can be written in the form

$$(\omega_{1,k}^2 - \omega^2) Q_1(\underline{k}) = -\sum_{\underline{k}} \Phi_{\underline{k},\underline{k}'}^{(1)} Q_1(\underline{k}') \tag{11}$$

where

$$\Phi_{\underline{k},\underline{k}'}^{(1)} = \frac{-2i}{Nm} \sum_\ell \{\exp-i(\underline{k}-\underline{k}')\cdot\underline{R}_\ell$$

$$\times [(\alpha_{\ell,\ell+1}-\alpha) \sin (k_x' a/2) \exp (i k_x' a/2)$$

$$(\alpha_{\ell,\ell+2}-\alpha) \sin (k_x' a/2) \exp (-i k_x' a/2)$$

$$+ (\beta_{\ell,\ell+3}-\beta) \sin (k_y' a/2) \exp (i k_y' a/2)$$

$$- (\beta_{\ell,\ell+4}-\beta) \sin (k_y' a/2) \exp (-i k_y' a/2)] \} . \tag{12}$$

The superscript (1) on $\Phi_{\underline{k},\underline{k}'}^{(1)}$ is used to indicate that polarizations along $\hat{x}$ only are included.

Equation (11) is identical in form to Langer's [2] Eq. (4) and Eq. (4) of (P-B). The three problems differ only in the form of the $\Phi_{\underline{k}, \underline{k}'}$. We shall follow the approach described in (P-B) because it is closer to the methods used here, although the basic technique was originally presented, and is more completely described, in Langer's paper.

For a particular configuration of springs, we can write

$$[D^{(1)}(\omega^2)]^{-1}_{\underline{k}, \underline{k}'} = (\omega^2_{\underline{k}} - \omega^2) \delta_{\underline{k}, \underline{k}'} + \Phi_{\underline{k}, \underline{k}'} \tag{13}$$

such that Eq. (11) becomes

$$\sum_{\underline{k}'} [D^{(1)}(\omega^2)]^{-1}_{\underline{k}, \underline{k}'} \, Q_1(\underline{k}') = 0 \ . \tag{14}$$

The spectral distribution function for this configuration, defined by

$$g(\omega) = \lim_{N \to \infty} \frac{2\omega}{N} \sum_n \delta(\Omega_n^2 - \omega^2) \ , \tag{15}$$

where the Ω_n are the exact eigenfrequencies for the particular configuration of springs, is given by [2]

$$g(\omega) = \frac{4\omega}{\pi} \lim_{\substack{N \to \infty \\ \epsilon \to 0}} \frac{1}{N} \, \text{Im Tr } D^{(1)}(\omega^2 + i\epsilon) \ . \tag{16}$$

In this expression, use of symmetry has made it unnecessary to include $D^{(2)}(\omega^2 + i\epsilon)$.

To obtain the spectral distribution function for the random distribution of springs, $\overline{g}(\omega)$, we must average the distribution function over all configurations which are consistent with a fixed value of q . As shown by

Langer, it is sufficient to take the configuration average, $\overline{D}^{(1)}(\omega^2 + i\epsilon)$, of $D^{(1)}(\omega^2 + i\epsilon)$. As in the one-dimensional problem, $\overline{D}^{(1)}(\omega^2 + i\epsilon)$ is diagonal in $\underline{k}$, so that

$$\overline{g}(\omega) = \frac{4\omega}{\pi} \lim_{\substack{N \to \infty \\ \epsilon \to 0}} \frac{1}{N} \text{ Im} \sum_{\underline{k}} \overline{D}_{\underline{k}}^{(1)}(\omega^2 + i\epsilon) . \tag{17}$$

B. Configuration Averages

As in (1), $D_{\underline{k}, \underline{k}'}^{(1)}(\omega^2)$ may be iterated to yield

$$D_{\underline{k}, \underline{k}'}^{(1)}(\omega^2) = \frac{1}{\omega_{\underline{k}}^2 - \omega^2} \left\{ \delta_{\underline{k}, \underline{k}'} - \frac{\Phi_{\underline{k}, \underline{k}'}^{(1)}}{\omega_{\underline{k}'}^2 - \omega^2} \right.$$

$$\left. + \sum_{\underline{k}'} \frac{\Phi_{\underline{k}, \underline{k}'}^{(1)} \Phi_{\underline{k}, \underline{k}'}^{(1)}}{(\omega_{\underline{k}_1}^2 - \omega^2)(\omega_{\underline{k}'}^2 - \omega^2)} + \ldots \right\} . \tag{18}$$

The average over configurations is performed at this point. Since the $\omega_{\underline{k}}$ are properties of the unperturbed lattice, it is only necessary to obtain configurational averages of the products $\Phi_{\underline{k}, \underline{k}_1}^{(1)} \Phi_{\underline{k}_1, \underline{k}_2}^{(1)} \Phi_{\underline{k}_2, \underline{k}_3}^{(1)} \cdots \Phi_{\underline{k}_n, \underline{k}'}^{(1)}$. We proceed to obtain these averages. The first, $\langle \Phi_{\underline{k}, \underline{k}'} \rangle$ is easily obtained. We need

$$< \Phi_{\underline{k}, \underline{k}'}^{(1)} > \; = \; \frac{(-2i)}{Nm} \; < \sum_{\ell} \; \exp -i \, (\underline{k} - \underline{k}') \cdot \underline{R}_{\ell}$$

$$x \; \{ \sin(k_x' a/2)[(\alpha_{\ell, \ell+1} - \alpha)\exp(ik_x' a/2) - (\alpha_{\ell, \ell+2} - \alpha)\exp(-ik_x' a/2)]$$

$$+ \sin(k_y' a/2)[(\beta_{\ell, \ell+3} - \beta)\exp(ik_y' a/2) - (\beta_{\ell, \ell+4} - \beta)\exp(-ik_y' a/2)] \} > . \qquad (19)$$

This expression is evaluated by keeping ℓ fixed while summing over configurations. No contribution to the terms linear in the α's is obtained from any configuration in which $\alpha_{\ell, \ell+1}$ or $\alpha_{\ell, \ell+2}$ is equal to α. The analogous situation holds for the terms linear in β. Denoting

$$\Delta\alpha = \alpha' - \alpha$$

and

$$\Delta\beta = \beta' - \beta , \qquad (20)$$

the configurational average is

$$< \Phi_{\underline{k}, \underline{k}'}^{(1)} > \; = \; \frac{(-2i)}{Nm} \sum_{\ell} \exp i \, (\underline{k}' - \underline{k}) \cdot \underline{R}_{\ell}$$

$$x \; q \, [2i\Delta\alpha\sin^2(k_x' a/2) + 2i \, \Delta\beta\sin^2(k_y' a/2)] . \qquad (21)$$

Performance of the summation over ℓ yields

$$< \Phi_{\underline{k}, \underline{k}'}^{(1)} > \; = (4q/m) \, [\Delta\alpha\sin^2(k_x' a/2) + \Delta\beta \sin^2(k_y' a/2)] \, \delta_{\underline{k}, \underline{k}'} \qquad (22)$$

Next, consider the second-order term

$$\langle \Phi^{(1)}_{\underline{k},\underline{k}_1} \Phi^{(1)}_{\underline{k},\underline{k}'} \rangle = \frac{(-2i)^2}{N^2 m^2} \sum_{\ell_1, \ell_2} \exp i (\underline{k}_1 - \underline{k}) \cdot \underline{R}_{\ell_1} \exp i (\underline{k}' - \underline{k}_1) \cdot \underline{R}_{\ell_2}$$

$$x \langle \{ \sin(k_{1x} a/2)[(\alpha_{\ell_1, \ell_1+1} - \alpha) \exp(ik_{1x} a/2) - (\alpha_{\ell_1, \ell_1+2} - \alpha) \exp(-ik_{1x} a/2)]$$

$$+ \sin(k_{1y} a/2)[(\beta_{\ell_1, \ell_1+3} - \beta) \exp(ik_{1y} a/2) - (\beta_{\ell_1, \ell_1+4} - \beta) \exp(-ik_{1y} a/2)] \}$$

$$x \{ \sin(k'_x a/2) [(\alpha_{\ell_2, \ell_2+1} - \alpha) \exp(ik'_x a/2) - (\alpha_{\ell_2, \ell_2+2} - \alpha) \exp(-ik'_x a/2)]$$

$$+ \sin(k'_y a/2)[(\beta_{\ell_2, \ell_2+3} - \beta) \exp(ik'_y a/2) - (\beta_{\ell_2, \ell_2+4} - \beta) \exp(-ik'_y a/2)] \} \rangle . \qquad (23)$$

As before, only terms in which the $\alpha_{i,j}$ and $\beta_{i,j}$ differ from α and β, respectively, contribute to the right-hand side of Eq. (23). In addition, as in (I-B), only the product terms in which the α_{i_1, j_1} and β_{i_1, j_1} represent the same springs as the α_{i_2, j_2} and β_{i_2, j_2}, respectively, contribute to first order in q. It should be noted that all the α-terms correspond to springs which are parallel to the direction (1), while all β-terms correspond to springs which are perpendicular to the direction (1). Thus, all product terms which involve both α's and β's must vanish, to first order in q, for a product of Φ's of any order. As a result of these considerations, we may write

$$< \Phi^{(1)}_{\underline{k}, \underline{k}_1} \ \Phi^{(1)}_{\underline{k}_1, \underline{k}'} > = \frac{(-2i)^2}{N^2 m^2} \sum_{\ell_1, \ell_2} \exp[i(\underline{k}_1 - \underline{k}) \cdot \underline{R}_{\ell_1}] \exp[i(\underline{k} - \underline{k}_1) \cdot \underline{R}_{\ell_2}]$$

$$\times \ \{ < [\alpha_{\ell_1, \ell_1+1} - \alpha) \exp (ik_{1x} a/2)$$

$$- (\alpha_{\ell_1, \ell_1+2} - \alpha) \exp (-ik_{1x} a/2)] \sin (k_{1x} a/2)$$

$$\times [(\alpha_{\ell_2, \ell_2+1} - \alpha) \exp (-ik'_x a/2)$$

$$- (\alpha_{\ell_2, \ell_2+2} - \alpha) \exp (-ik'_x a/2)] \sin (k'_x a/2) >$$

$$+ <(\beta_{\ell_1, \ell_1+3} - \beta) \exp (ik_{1y} a/2)$$

$$- (\beta_{\ell_1, \ell_1+4} - \beta) \exp (-ik_{1y} a/2)] \sin (k_{1y} a/2)$$

$$\times [(\beta_{\ell_2, \ell_2+3} - \beta) \exp (ik'_y a/2)$$

$$- (\beta_{\ell_2, \ell_2+4} - \beta) \exp (-ik'_y a/2)] \sin (k'_y a/2) > \} \ . \tag{24}$$

The important feature of Eq. (24) which makes this problem soluble
is that the two-dimensional average of Eq. (23) has been split into two one-
dimensional averages which are mathematically identical to those which
have been evaluated in (P-B). This splitting occurs, for terms which are
first order in q , for all order products of the Φ's. As a result, using
Eq. (30) of (P-B), we obtain the general expression

$$< \Phi_{\underline{k}, \underline{k}_1}^{(1)} \Phi_{\underline{k}_1, \underline{k}_2}^{(1)} \cdots \cdots \Phi_{\underline{k}_{n-1}, \underline{k}_n}^{(1)} >$$

$$= \frac{q\, \delta_{\underline{k}, \underline{k}_n}}{N^{n-1}} \left(\frac{4}{m} \right)^n \left[(\Delta \alpha)^n \sin^2 \left(\frac{k_{1x} a}{2} \right) \sin^2 \left(\frac{k_{2x} a}{2} \right) \cdots \sin^2 \left(\frac{k_{nx} a}{2} \right) \right.$$

$$\left. + (\Delta \beta)^n \sin^2 \left(\frac{k_{1y} a}{2} \right) \sin^2 \left(\frac{k_{2y} a}{2} \right) \cdots \sin^2 \left(\frac{k_{ny} a}{2} \right) \right]. \tag{25}$$

C. Calculation of the Elastic Spectrum

The form of Eq. (25) indicates, as expected, that $\overline{D}^{(1)}$ is diagonal in $\underline{k}$. As a result, we may follow Langer and write the diagonal elements of $\overline{D}^{(1)}$ as $D_{\underline{k}}^{(1)}$ where

$$D_{\underline{k}}^{(1)}(\omega^2) = \frac{1}{\omega_{\underline{k}}^2 - \omega^2 + G_{\underline{k}}^{(1)}(\omega^2)} . \tag{26}$$

The configuration average of Eq. (18) may then be rewritten, using Eqs. (25) and (26) as

$$G_{\underline{k}}^{(1)} = q \sum_n \frac{(-1)^{r-1} (4)^n}{N^{n-1} m^n} \left[(\Delta \alpha)^n \sin^2 \left(\frac{k_x a}{2} \right) \left(\sum_{\underline{k}_1} \frac{\sin^2 (k_{1x} a/2)}{\omega_{1,\underline{k}}^2 - \omega^2} \right)^{n-1} \right.$$

$$\left. + (\Delta \beta)^n \sin^2 \left(\frac{k_y a}{2} \right) \left(\sum_{\underline{k}_1} \frac{\sin^2 (k_{1y} a/2)}{\omega_{1,\underline{k}}^2 - \omega^2} \right)^{n-1} \right] . \tag{27}$$

Since there are no terms in which both $\Delta\alpha$ and $\Delta\beta$ appear, Eq. (27) is easily transformed into the expression

$$
G_{\underline{k}}^{(1)} = \frac{[4q(\Delta\alpha)/m]\,\sin^2\,(k_x a/2)}{1 + \dfrac{4\,(\Delta\alpha)}{mN}\displaystyle\sum_{\underline{k}_1}\dfrac{\sin^2(k_{1x}a/2)}{\omega^2_{1,\,\underline{k}_1} - \omega^2}}
$$

$$
+ \frac{[4q\,(\Delta\beta)/m]\,\sin^2(k_y a/2)}{1 + \dfrac{4\,(\Delta\beta)}{mN}\displaystyle\sum_{\underline{k}_1}\dfrac{\sin^2(k_{1y}a/2)}{\omega^2_{1,\,\underline{k}_1} - \omega^2}} \,. \tag{28}
$$

The entire problem is then reduced to an evaluation of the summations

$$
I = \frac{i}{N}\sum_{\underline{k}}\frac{\sin^2(k_x a/2)}{\omega^2_{1,\,\underline{k}} - \omega^2} \,, \tag{29}
$$

and

$$
J = \frac{1}{N}\sum_{\underline{k}}\frac{\sin^2\,(k_y a/2)}{\omega^2_{1,\,\underline{k}} - \omega^2} \,. \tag{30}
$$

Because of the symmetry associated with this lattice,

$$
I\,(\alpha,\,\beta) = J\,(\beta,\,\alpha) \,. \tag{31}
$$

Eq. (31) implies that one need evaluate Eq. (29) only. Transforming the right-hand side of Eq. (29) into an integral, we obtain

$$
I = \lim_{\epsilon\to 0}\frac{a^2}{4\pi}\int_{-\pi/a}^{\pi/a}\int_{-\pi/a}^{\pi/a}\frac{\sin^2\,(k_x a/2)\,dk_x\,dk_y}{(4\alpha/m)\sin^2(k_x a/2) + (4\beta/m)\,\sin^2\,(k_y a/2)-\omega^2-i\epsilon} \,. \tag{32}
$$

In Appendix I, it is shown that the value of this integral is given by

$$I = (m/2\pi\alpha)\tan^{-1}(\alpha/\beta)^{1/2} + (im^2\omega^2/32\alpha\beta)(\beta/\alpha)^{1/2} \tag{33}$$

under the conditions

$$m\omega^2/4\alpha \ll 1$$

and

$$m\omega^2/4\beta \ll 1 . \tag{34}$$

These conditions limit our discussion to the elastic portion of the spectrum. It would be reasonably simple. but tedious, to obtain higher order terms in the ω^2 power series expansion of I. Since interesting physical results are obtained from the lowest order terms, we shall not continue the procedure, but shall continue with the determination of the elastic portion of the spectrum.

Substitution of Eq. (33) into Eq. (31) yields

$$J = (m/2\pi\beta)\tan^{-1}(\beta/\alpha)^{1/2} + (im^2\omega^2/32\alpha\beta)(\alpha/\beta)^{1/2} . \tag{35}$$

Substitution of Eqs. (31) and (33) into Eq. (28) yields

$$G_k^{(1)} = \frac{(4q\Delta\alpha/m)\sin^2(k_x a/2)}{1 + (2\Delta\alpha/\pi\alpha)\tan^{-1}(\alpha/\beta)^{1/2} + (im\omega^2\Delta\alpha/8\alpha\beta)(\beta/\alpha)^{1/2}}$$

$$+ \frac{(4q\Delta\beta/m)\sin^2(k_y a/2)}{1 + (2\Delta\beta/\pi\beta)\tan^{-1}(\beta/\alpha)^{1/2} + (im\omega^2\Delta\beta/8\alpha\beta)(\alpha/\beta)^{1/2}} . \tag{36}$$

As in one-dimension [1, 2] we may associate the positions of the poles of the function $D_{\underline{k}}^{(1)}(\omega^2)$ with the modes of vibration of the lattice with the randomly distributed impurity springs. The frequencies, for each $\underline{k}$, and with polarization vector parallel to $\hat{x}$, are given by the real part of the roots of the equation

$$\omega_{\underline{k}}^2 - \omega^2 + G_{\underline{k}}^{(1)}(\omega^2) = 0 . \tag{37}$$

A complete solution of $G_{\underline{k}}^{(1)}(\omega^2)$ would lead to a number of roots, for fixed $\underline{k}$, of Eq. (37). The existence of these roots is a mirror of the fact that $\underline{k}$, for any one member of the ensemble, is not a good label. By restricting our calculation of $G_{\underline{k}}^{(1)}(\omega^2)$ to small ω^2, and keeping terms of lowest order only in the resulting small parameters, we have suppressed the multiplicity of these roots. The resulting expression for the elastic mode frequencies is given by

$$\omega_1^2 = \frac{4\alpha}{m} \left[1 + \frac{q\,(\Delta\alpha)}{\alpha + (2/\pi)(\Delta\alpha)\tan^{-1}(\alpha/\beta)^{1/2}} \right] \sin^2(k_x a/2)$$

$$+ \frac{4\beta}{m} \left[1 + \frac{q\,(\Delta\beta)}{\beta + (2/\pi)(\Delta\beta)\tan^{-1}(\beta/\alpha)^{1/2}} \right] \sin^2(k_y a/2) . \tag{38}$$

The solution of Eq. (37) also contains an imaginary part. Writing the solution as

$$\omega = \omega_{1,\underline{k}} + \Delta_{1,\underline{k}} - i\Gamma_{1,\underline{k}} , \tag{39}$$

the imaginary part

$$\Gamma_{1,\underline{k}} = \frac{q\,\omega_{\underline{k}}}{4\,(\alpha\beta)^{1/2}} \left\{ \frac{(\Delta\alpha)^2 \sin^2(k_x a/2)}{\alpha\,[1+(2\Delta\alpha/\pi\alpha)\tan^{-1}(\alpha/\beta)^{1/2}]^2} \right.$$

$$\left. + \frac{(\Delta\beta)^2 \sin^2(k_y a/2)}{\beta\,[1+(2\Delta\beta/\pi\beta)\tan^{-1}(\beta/\alpha)^{1/2}]^2} \right\} \quad , \tag{40}$$

corresponds [1] to the reciprocal of the lifetime of the mode. It should be
noted that $\Gamma_{1,\underline{k}}$ is of one order higher in the small parameters of Eq. (34)
than is $\Delta_{1,\underline{k}}$. Thus, although the low frequency modes are shifted in frequency,
they are quite well defined.

Finally, the density of states, $\bar{g}(\omega)$, as indicated in Eq. (17), and
calculated in Appendix II, is given by the expression

$$\bar{g}(\omega) = \frac{\omega m}{\pi\,(\bar{\alpha}\bar{\beta})^{1/2}} \quad . \tag{41}$$

Here, $\bar{\alpha}$ and $\bar{\beta}$ are defined by Eqs. (57) and (58). These results will be
discussed in Section V, after the analogous expressions have been obtained
for the isotopic impurity problem.

IV. THE ISOTOPIC IMPURITY PROBLEM

A. Formulation

In this problem, the unperturbed lattice is again the square lattice
discussed in Section II. In this case, the Nq atoms at randomly positioned
sites are replaced by isotopes of mass m'. The mass of the isotope at
site l is denoted by m_l. The equation of motion of the atom at this site
is given by

$$-\omega^2 \begin{pmatrix} x_{\ell,1} \\ x_{\ell,2} \end{pmatrix} + \frac{1}{m} \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+1,1} \\ x_{\ell,2} - x_{\ell+1,2} \end{pmatrix} + \frac{1}{m} \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+2,1} \\ x_{\ell,2} - x_{\ell+2,2} \end{pmatrix}$$

$$+ \frac{1}{m} \begin{pmatrix} \beta & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+3,1} \\ x_{\ell,2} - x_{\ell+3,2} \end{pmatrix} + \frac{1}{m} \begin{pmatrix} \beta & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+4,1} \\ x_{\ell,2} - x_{\ell+4,1} \end{pmatrix}$$

$$= \left(\frac{1}{m} - \frac{1}{m_\ell} \right) \left\{ \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+1,1} \\ x_{\ell,2} - x_{\ell+1,2} \end{pmatrix} + \begin{pmatrix} \alpha & 0 \\ 0 & \beta \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+2,1} \\ x_{\ell,2} - x_{\ell+2,2} \end{pmatrix} \right.$$

$$\left. + \begin{pmatrix} \beta & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+3,1} \\ x_{\ell,2} - x_{\ell+3,2} \end{pmatrix} + \begin{pmatrix} \beta & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} x_{\ell,1} - x_{\ell+4,1} \\ x_{\ell,2} - x_{\ell+4,2} \end{pmatrix} \right\} . \tag{42}$$

As in Section III, the x and y components of the motion are completely decoupled, and may be considered separately. As a result of symmetry, it is sufficient to consider the x-component motion for a complete quadrant of the space of the propagation vector, $\underline{k}$. The transformation to the normal coordinates of the unperturbed system, Eq. (7), yields the equation of motion,

$$-\omega^2 \sum_{\underline{k}} Q_1(\underline{k}) \exp i \underline{k} \cdot \underline{R}_\ell + (\alpha/m) \sum_{\underline{k}} [2 - \exp(ik_x a) - \exp(-ik_x a)] Q_1(\underline{k}) \exp i \underline{k} \cdot \underline{R}_\ell$$

$$+ (\beta/m) \sum_{\underline{k}} [2 - \exp(ik_y a) - \exp(-ik_y a)] Q_1(\underline{k}) \exp i \underline{k} \cdot \underline{R}_\ell$$

$$= \sum_{\underline{k}} Q_1(\underline{k}) [(1/m) - (1/m_\ell)] \exp i \underline{k} \cdot \underline{R}_\ell [\alpha (2 - \exp i k_x a - \exp - i k_x a)$$

$$+ \beta (2 - \exp i k_y a - \exp - i k_y a)] . \tag{43}$$

Equation (43) is similar in form to Eq. (9). By mathematical manipulations which are similar to those which lead from Eq. (9) to Eq. (11), Eq. (43) is transformed into

$$(\omega_{1,\underline{k}}^{2} - \omega^{2})\, Q_{1}(\underline{k}) = -\sum_{\underline{k}'} Q_{1}(\underline{k}')\, \Phi_{\underline{k},\underline{k}'} \quad , \tag{44}$$

where

$$\Phi_{\underline{k},\underline{k}'} = \frac{\omega_{1,\underline{k}'}}{N} \sum_{\ell} (\frac{m}{m_{\ell}} - 1)\, \exp\, i\, (\underline{k}' - \underline{k}) \cdot \underline{R}_{\ell} \quad . \tag{45}$$

This result is identical to that obtained by Langer [2] for the one-dimensional problem. It is easily shown that the entire difference between the two problems is represented in the form of the function $G_{\underline{k}}^{(1)}(\omega^{2})$ which, for this problem, is given by

$$G_{\underline{k}}^{(1)}(\omega^{2}) = \cfrac{q\lambda\omega_{1,\underline{k}}^{2}}{1 + \cfrac{\lambda}{N}\sum_{\underline{k}'} \cfrac{\omega_{1,\underline{k}'}^{2}}{\omega_{1,\underline{k}'}^{2} - \omega^{2}}} \tag{46}$$

where

$$\lambda = (m/m') - 1 \quad , \tag{47}$$

The remainder of the problem consists of the evaluation of the sum

$$\sum_{\underline{k}'} \frac{\omega_{1,\underline{k}'}^{2}}{\omega_{1,\underline{k}'}^{2} - \omega^{2}} = \frac{4\alpha}{m} \sum_{\underline{k}'} \frac{\sin^{2}(k_{x}'a/2)}{\omega_{1,\underline{k}'}^{2} - \omega^{2}}$$

$$+ \frac{4\beta}{m} \sum_{\underline{k}'} \frac{\sin^{2}(k_{y}'a/2)}{\omega_{1,\underline{k}'}^{2} - \omega^{2}} \quad . \tag{48}$$

The two sums which appear on the right-hand side of Eq. (48) have been evaluated in the Appendix I and have been used in Section III, for the case where Eq. (34) holds. Substituting Eqs. (33) and (35) into Eq. (48), and inserting the result into Eq. (46), one obtains the result

$$G_{\underline{k}}^{(1)}(\omega^2) = q\lambda \omega_{1,\underline{k}}^2 \{1 + \lambda [1 + (i\omega^2 m/(\alpha\beta)^{1/2}]\}^{-1} . \tag{49}$$

With this result, it is easily shown that the frequencies of propagation, in the elastic limit, are given by the expression

$$\omega^2 = \omega_{1,\underline{k}}^2 (1 + q\kappa) , \tag{50}$$

where

$$\kappa = 1 - (m'/m) . \tag{51}$$

The inverse lifetimes are given by

$$\Gamma_{\underline{k}}^{(1)} = \frac{q\lambda^2 m \omega_{1,\underline{k}}^2}{2(1+\lambda)^2 (\alpha\beta)^{1/2}} . \tag{52}$$

Before leaving this problem, we should point out that another aspect of it has been treated by Mahanty, Maradudin, and Weiss [3]. They considered the local modes which arise when m' < m. Many of the mathematical difficulties, which these authors surmounted quite elegantly, have been avoided in this work because attention was restricted to the elastic spectrum.

V. DISCUSSION -- THE VIRTUAL CRYSTAL APPROXIMATION

One frequently finds statements in the literature that the so-called "virtual crystal approximation" must hold for the elastic spectrum of a crystal containing a small number of impurities, or a small degree of disorder. In

this approximation, the masses are all taken as the average mass, and the
spring constants are all taken as the average spring constant. The justification
given for this approximation is usually that the wavelengths of the modes are
very long compared to the range of the local perturbations, so that these
perturbations are just averaged. Other authors have carried the approximation
further, and have concluded that the failure of the virtual crystal approximation
to explain the vibrational frequencies near the Brillouin zone surface, of
dilute alloys, is evidence for the existence of short-range order in these
alloys. In this section, we examine this approximation with the aid of the
solutions obtained in the preceding sections.

The two one-dimensional solutions obtained previously [1, 2] yield
virtual crystal approximation-type results to first order in q . Langer [1]
finds that the elastic spectrum of a system with isotopic impurities is
completely described by an average mass given by

$$\overline{m} = (1-q)m + qm' .\qquad\qquad(53)$$

In (P-B), the authors find that it is the inverse of the spring constant
which must be averaged. That is, taking γ as the nearest-neighbor spring
constant of the unperturbed system, and γ' as the spring constant which
replaces it at randomly positioned sites, the elastic spectrum is completely
described by an effective spring constant, $\overline{\gamma}$, which is given by the expression

$$1/\overline{\gamma} = [(1-q)/\gamma] + (q/\gamma') .\qquad\qquad(54)$$

Henceforth, we shall speak of this equation as the virtual crystal approximation
for spring impurities.

For the isotopic substitution in two dimensions, the situation is quite
similar. Equation (50) can be rewritten as

$$\omega^2 = m\,\omega_{1,\underline{k}}^2\,[m(1-q) + q\,m']^{-1} \tag{55}$$

to first order in q. Since $m\,\omega_{1,\underline{k}}^2$ is independent of mass, this is the result
expected from the virtual crystal approximation.

There is good reason to believe that the approximation must hold for
the elastic spectrum of a system of any dimensionality and any concentration
where the only substitutions are isotopic and the system is homogeneous on a
macroscopic scale. The reasoning goes as follows. The masses enter the
dynamical equation through acceleration terms only. Thus, they do not
contribute at all to the static elastic constants, which depend only on the
interactions. The only way that the masses enter into the classical expressions
for the elastic spectrum is through the density, since the elastic spectrum
is, of course, entirely determined, for a homogeneous solid, by a knowledge
of the elastic constants and the density. Thus, the only condition for the
applicability of the virtual crystal approximation to the elastic spectrum of
an isotope-substituted system is that it be homogeneous. That is, one must
be able to divide the crystal into volume elements whose dimensions are small
compared to the wavelength of the elastic modes, all of which have the same
density associated with them. In this case, the virtual crystal approximation
is just a means of calculating that density.

The argument just presented leads one to suspect that it is in the case where the spring constants are changed that one expects a breakdown of the approximation. This is the case. For comparison, we may rewrite Eq. (54) as

$$\overline{\gamma} = \gamma \left[1 + q \Delta \gamma / (\gamma + \Delta \gamma) \right] . \tag{56}$$

Comparison of Eq. (38), for the perturbed system, with Eq. (4) for the unperturbed system, shows that one can define effective force constants, $\overline{\alpha}$ and $\overline{\beta}$, by the relations

$$\overline{\alpha} = \alpha \left[1 - \frac{q \Delta \alpha}{\alpha + \Delta \alpha (2/\pi) \tan^{-1} (\ /\beta)^{1/2}} \right] \tag{57}$$

and

$$\overline{\beta} = \beta \left[1 + \frac{q \Delta \beta}{\beta + \Delta \beta (2/\pi) \tan^{-1} (\beta /\alpha)^{1/2}} \right] . \tag{58}$$

These results indicate immediately that a knowledge of q, α and α' is not sufficient to define $\overline{\alpha}$. The relationship between α and β also enters into the expression for $\overline{\alpha}$. The same is true for $\overline{\beta}$.

The reasons for this dependence can be visualized easily. Consider Fig. 1, which portrays the displacements of atoms in the region of an impurity spring from equilibrium while participating in a longitudinal mode. Here, we have taken $\alpha' > \alpha$. The intersections of the dashed lines represent the equilibrium positions. The straight vertical lines represent the lines of constant phase associated with the mode of the unperturbed system. Atoms 1 and 2 are connected by a spring which is stronger, and which prevents them

from separating by the distance associated with the unperturbed mode. As
a result, there is a shear component in the motion of, say, atom 1 with
respect to atoms 3 and 5, and the shear constant β enters into the frequency
of a mode whose frequency is determined entirely by α in the unperturbed
system. Some of the relationships of this picture to the mathematical solution,
Eq. (57), are easily seen. We note, first of all, that this is a calculation to
first order in q . Thus, we can neglect other "wrong" springs. As a result,
the picture indicates that there is no shear motion of atom 1 with respect to
atom 2. Thus, β' does not enter into the expression for $\bar{\alpha}$. Similarly, we
would expect, from this picture, that the virtual crystal approximation would
hold for $\bar{\alpha}$ if $\beta = 0$. This is the case, since $(2/\pi) \tan^{-1}(\infty) = 1$, making
Eq. (57) identical to Eq. (56). Setting $\beta = 0$ also has the effect, of course,
of making the lattice unstable. Finally, we may look at the problem as the
picture does, with a classical perturbation theory viewpoint, treating $(\Delta\alpha)$
as the perturbation on this mode. In first order, the energy shift is obtained
by letting the system undergo its unperturbed motion. In this order, β should
not appear. It is only in second order, when the motion has been changed to
first order, that the effect of β should enter in. It is readily seen from
Eq. (57) that β only enters into terms of second and higher order in $\Delta\alpha$.

Equations (57) and (58) do show that the two virtual crystal approximations
which may be used to obtain average spring constants form upper and lower
bounds for the actual $\bar{\alpha}$ and $\bar{\beta}$, for the model discussed here. The
$\tan^{-1}(\alpha/\beta)^{1/2}$ and $\tan^{-1}(\beta/\alpha)^{1/2}$ in these equations have upper and lower

bounds of 0 and $\pi/2$. For $\tan^{-1}(\beta/\alpha)^{1/2} = 0$, these equations become

$$1/\bar{\alpha} = [(1-q)/\alpha] + [q/\alpha'] \tag{59}$$

and

$$\bar{\beta} = (1-q)\beta + q\beta' . \tag{60}$$

For $\tan^{-1}(\beta/\alpha)^{1/2} = \pi/2$, of course, the situations are reversed. Equation (59) corresponds to the $1/\gamma$ averaging which was obtained in one dimension, while Eq. (60) is the straightforward averaging of the spring constants. Any intermediate values of $\tan^{-1}(\beta/\alpha)^{1/2}$ will yield results which lie between the two simple forms of averaging. Note that this discussion has been restricted to the cases where $\Delta\alpha/\alpha > -1$ and $\Delta\beta/\beta > -1$. These conditions must be satisfied if each atom has its motion centered about a position of stable equilibrium in the static crystal.

Paul [4] has obtained the identical upper and lower bounds for the elastic constants of isotropic multiphase materials. He shows that such bounds hold in general in the situation where "... the constituents are distinct and capable of separation by purely mechanical means (e.g., not solid solutions)". In the language of lattice dynamics, Paul is restricting his work to situations in which the force constants between atoms belonging to the interiors of different constituents are zero. That is, the elastic constants associated with each of the constituents completely describe the interactions. This situation is quite similar to that discussed here. In the determination of the elastic constants, it is only the pairwise interactions, and not the masses, which are significant. Thus, since nearest neighbor interactions only are

considered, we may consider each impurity spring as an independent constituent, and the results are consistent with Paul's bounds. For some reason that we do not understand, the fact that the system is not isotropic does not seem to be important in this case. This analysis raises the possibility, however, that important and interesting effects may appear when longer range interactions appear.

Figure 2 shows the deviations of $\bar{\alpha}$ and $\bar{\beta}$, as given by Eqs. (57) and (58), from the virtual crystal approximation. In these graphs, we have taken $\alpha/\beta = 9$. This ratio was obtained from the elastic constants of β-brass, as measured by McManus [5] by setting $\alpha/\beta = C_{11}/[(C_{11}-C_{12})/2]$. As expected, $\bar{\alpha}$ lies close to the curve defined by Eq. (59), while $\bar{\beta}$ is given, approximately, by Eq. (60). A choice of $\alpha/\beta \approx 1$, corresponding to a strongly covalent crystal, would lead to lines for $\bar{\alpha}$ and $\bar{\beta}$ which have slopes, at $q = 0$ and 1, that are approximately equal to the average of the slopes associated with the two virtual crystal approximations.

Since $\bar{\alpha}$ and $\bar{\beta}$ also determine, through Eq. (41), the spectral distribution function for small ω^2, the remarks about $\bar{\alpha}$ and $\bar{\beta}$ apply to it as well.

Finally, it is important to note that the random spring calculation performed in this work applied specifically to the order-disorder problem. There exists another interesting related situation which remains to be treated. It is the case where impurity atoms, which are substituted into the two-dimensional lattice, have approximately the same mass as the solvent

atoms, but change the spring constants. In this case, the four sets of spring constants associated with the interaction of the impurity atom with each of its neighbors must appear together in the averaging. Work is underway on this problem, and it is expected that the results will soon be presented. The results obtained here indicate that it is highly likely that the virtual crystal approximations are inadequate for the description of the modifications of the elastic spectrum of such a system. If this is the case, any attempt to assign observed breakdowns of the approximation to ordering or clustering, without corroborative diffraction evidence, would appear unjustified. This is particularly true when the modes are not a portion of the elastic spectrum, but are associated with the Brillouin zone surface.

VI. ACKNOWLEDGMENTS

APPENDIX I

EVALUATION OF THE INTEGRAL OF EQUATION (32)

The value of the integral

$$I = \lim_{\epsilon \to 0} \int_{-\pi/a}^{\pi/a} \int_{-\pi/a}^{\pi/a} \frac{\sin^2(k_x a/2) \, dk_x \, dk_y}{(4\alpha/m)\sin^2(k_x a/2) + (4\beta/m)\sin^2(k_y a/2) - \omega^2 - i\epsilon} \tag{A-1}$$

is required in the limits $\omega^2 \ll 4\alpha/m$ and $\omega^2 \ll 4\beta/m$. We begin by fixing k_y and evaluating the integral over k_x. Consider the case $\omega^2 > (4\beta/m)\sin^2(k_y a/2)$. Let

$$\omega'^2 = \omega^2 - (4\beta/m)\sin^2(k_y a/2) , \tag{A-2}$$

and

$$I_1 = \int_{-\pi/a}^{\pi/a} \frac{\sin^2(k_x a/2) \, dk_x}{(4\alpha/m)\sin^2(k_x a/2) - \omega'^2 - i\epsilon} . \tag{A-3}$$

Letting

$$z = \exp i k_x a , \tag{A-4}$$

$$\omega''^2 = (m/\alpha)\omega'^2 , \tag{A-5}$$

and

$$\epsilon'' = (m/\alpha)\epsilon , \tag{A-6}$$

Eq. (A-3) becomes

$$I_1 = \frac{m}{4\alpha a i} \oint \frac{(z-1)^2 \, dz}{z \left[z^2 - (2 - \omega''^2 - i\epsilon'')z + 1 \right]} , \tag{A-7}$$

where the contour of integration is the unit circle. The denominator of the integrand has three roots,

$$z_0 = 0 , \tag{A-8}$$

$$z_1 = (1 - \tfrac{1}{2}\omega''^2 - \tfrac{1}{2} i\epsilon'') + i \left[1 - (1 - \tfrac{1}{2}\omega''^2 - \tfrac{1}{2} i\epsilon'')^2 \right]^{1/2} \tag{A-9}$$

$$z_2 = (1 - \tfrac{1}{2}\omega''^2 - \tfrac{1}{2} i\epsilon'') - i \left[1 - (1 - \tfrac{1}{2}\omega''^2 - \tfrac{1}{2} i\epsilon'')^2 \right]^{1/2} \tag{A-10}$$

Since $\omega''^2 < 1$, z_1 is inside and z_2 is outside the unit circle. Thus, we obtain the solutions

$$I_1 = \frac{m\pi}{2\alpha a} \left\{ \frac{1}{z_1 z_2} + \frac{(z_1 - 1)^2}{z_1 (z_1 - z_2)} \right\} . \tag{A-11}$$

Evaluating Eq. (A-11) in terms of the variables of Eq. (A-1), we obtain

$$I_1 = \frac{m\pi}{2\alpha a} \left\{ 1 + \frac{i (\beta/\alpha)^{1/2} [(m\omega^2/4\beta) - \sin^2(k_y a/2)]^{1/2}}{[1 - (m\omega^2/4\alpha) + (\beta/\alpha) \sin^2(k_y a/2)]^{1/2}} \right\} . \tag{A-12}$$

In a similar manner, we consider the case $\omega^2 < (4\beta/m) \sin^2(k_y a/2)$.

Letting $\omega'^2 = (4\beta/m) \sin^2(k_y a/2) - \omega^2 ,$ \hfill (A-13)

we obtain the integral

$$I_2 = \int_{-\pi/a}^{\pi/a} \frac{\sin^2(k_x a/2)\, dk_x}{(4\alpha/m)\sin^2(k_x a/2) + \omega'^2}$$

$$= \frac{m\pi}{2\alpha a} \left\{ 1 - \frac{(\beta/\alpha)^{1/2} [\sin^2(k_y a/2) - (\omega^2 m/4\beta)]^{1/2}}{[1 + (\beta/\alpha)\sin^2(k_y a/2) - (\omega^2 m/4\alpha)]^{1/2}} \right\} . \tag{A-14}$$

Substitution of Eqs. (A-12) and (A-14) into Eq. (A-1) yields the expression

$$I = \frac{am}{8\pi\alpha} \int_{-\pi/a}^{\pi/a} dk_y$$

$$+ \frac{iam}{4\pi\alpha} \int_{0}^{(2/a)\sin^{-1}(m\omega^2/4\beta)^{1/2}} \frac{(\beta/\alpha)^{1/2}[(\omega^2 m/4\beta)-\sin^2(k_y a/2)]^{1/2}dk_y}{[1-(m\omega^2/4\alpha)+(\beta/\alpha)\sin^2(k_y a/2)]^{1/2}}$$

$$- \frac{am}{4\pi\alpha} \int_{(2/a)\sin^{-1}(m\omega^2/4\beta)^{1/2}}^{\pi/a} \frac{(\beta/\alpha)^{1/2}[\sin^2(k_y a/2)-(\omega^2 m/4\beta)]^{1/2} dk_y}{[1+(\beta/\alpha)\sin^2(k_y a/2)-(\omega^2 m/4\alpha)]^{1/2}} \, .$$

$$(A-15)$$

It should be noted at this time that the integrands are all real. Thus, the first and third terms of the right-hand side of Eq. (A-15) contribute the real part of I, while the second term yields the imaginary part.

For convenience, we denote:

$$I_3 = (am/8\pi\alpha) \int_{-\pi/a}^{\pi/a} dk_y = m/4\alpha \, , \qquad (A-16)$$

$$I_4 = \frac{iam}{4\pi\alpha} \left(\frac{\beta}{\alpha}\right)^{1/2} \int_{0}^{(2/a)\sin^{-1}(m\omega^2/4\beta)^{1/2}} \frac{[(m\omega^2/4\beta)-\sin^2(k_y a/2)]^{1/2} dk_y}{[1-(m\omega^2/4\alpha)+(\beta/\alpha)\sin^2(k_y a/2)]^{1/2}} \, ,$$

$$(A-17)$$

$$I_5 = \frac{am}{4\pi\alpha} \left(\frac{\beta}{\alpha}\right)^{1/2} \int_{(2/a)\sin^{-1}(m\omega^2/4\beta)^{1/2}}^{\pi/a} \frac{[\sin^2(k_y a/2)-(m\omega^2/4\beta)]^{1/2} dk_y}{[1-(m\omega^2/4\alpha)+(\beta/\alpha)\sin^2(k_y a/2)]^{1/2}} \, .$$

$$(A-18)$$

Let

$$t = \sin(k_y a/2) ,$$

$$\delta = (m\omega^2/4\beta) \ll 1 ,$$

and

$$\delta' = (m\omega^2/4\alpha) \ll 1 . \tag{A-19}$$

Then Eq. (A-17) can be written as

$$I_4 = \frac{ima^2}{8\pi\alpha}(\frac{\beta}{\alpha})^{1/2} \int_0^{(\delta)^{1/2}} \frac{(\delta - t^2)^{1/2}\,dt}{[1-\delta' + (\beta/\alpha)t^2]^{1/2}[1-t^2]^{1/2}} . \tag{A-20}$$

It is easily seen that $t \ll 1$ over the range of integration. Thus, we may approximate the entire denominator of the integrand of Eq. (A-20) by unity to obtain an expression which is good to only first order in δ and δ'. In this case we may write

$$I_4 \approx \frac{im}{2\pi\alpha}(\frac{\beta}{\alpha})^{1/2} \int_0^{(\delta)^{1/2}} (\delta - t^2)^{1/2}\,dt$$

$$= \frac{im^2\omega^2}{32\alpha\beta}(\frac{\beta}{\alpha})^{1/2} . \tag{A-21}$$

Substitution of Eq. (A-19) into Eq. (A-18) yields the expression

$$I_5 = \frac{m}{2\pi\alpha}(\frac{\beta}{\alpha})^{1/2} \int_{(\delta)^{1/2}}^{1} \frac{(t^2 - \delta)^{1/2}\,dt}{[1-t^2]^{1/2}[1-\delta'+(\beta/\alpha)t^2]^{1/2}} . \tag{A-22}$$

In this case, the approximations are less straightforward. It is clear that δ' may be set equal to zero, since it is always very much less than the other terms contained in the radical in which it appears. Further

simplification of the integrand is hindered by the fact that $\delta/t^2 \approx 1$ near the

lower limit of integration. Nevertheless, we may write $[1-(\delta/t^2)]^{1/2} \approx 1$ in

the integrand for the reasons which follow. The factor $[1+(\beta/\alpha)t^2]^{1/2}$ of the

denominator is a relatively slowly varying function. As a result, the remainder

of the integrand is sharply peaked near the upper limit of integration. In this

region, it   lite reasonable to replace the radical of the numerator by unity.

Hence, if $_5$ contained the entire contribution to the real part of I, it would

be sufficient to make this replacement. Unfortunately, however, a major

portion of I_5 is cancelled by I_3. Thus, it is necessary to justify this replace-

ment a bit more carefully. We do this by calculating an upper and lower bound

to the integral. It is then shown that the difference between the two is negligible

compared to the real part of I. To compute these bounds, we note that the

integrand is positive and real over the range of integration. In addition, over

this range, $[1-(\delta/t^2)] \le [1-(\delta/t^2)]^{1/2} \le 1$. Thus, lower and upper bounds to the

integral can be obtained by using the upper and lower bounds of the radical

in the integrand. To obtain the values of the associated integrals, we need

$$\frac{m}{2\pi\alpha} (\frac{\beta}{\alpha})^{1/2} \int_{(\delta)^{1/2}}^{1} \frac{t \, dt}{[1-t^2]^{1/2} [1+(\beta/\alpha)t^2]^{1/2}}$$

$$= \frac{m}{4\alpha} - \frac{m}{2\pi\alpha} \tan^{-1} (\frac{\alpha}{\beta})^{1/2} + O(\delta) , \qquad\qquad (A\text{-}23)$$

and

$$
\frac{m\delta}{2\pi\alpha}\,(\frac{\beta}{\alpha})^{1/2}\int_{(\delta)^{1/2}}^{1}\frac{dt}{t\,[1-t^2]^{1/2}\,[1+(\beta/\alpha)\,t^2]^{1/2}}
$$

$$
=\;\frac{m\delta}{4\pi\alpha}\,(\frac{\beta}{\alpha})^{1/2}\,\log\left\{\frac{[\alpha+(\beta-\alpha)\,\delta-\beta\delta^2]^{1/2}+\alpha}{\delta\,(\alpha)^{1/2}}\;+\;\frac{(\beta-\alpha)}{2\alpha}\right\}
$$

$$
-\;\frac{m\delta}{4\pi\alpha}(\frac{\beta}{\alpha})^{1/2}\,\log\left[\frac{(\beta-\alpha)}{2\alpha}\right]\,. \tag{A-24}
$$

Equation (A-24) shows clearly that the difference between the upper and lower bounds is of the order of $\delta\log\delta$. This should be compared with the result for I, obtained by using Eq. (A-23) for I_5, and substituting the results of Eqs. (A-16) and (A-21) into Eq. (A-15). We get

$$
I\;=\;\frac{m}{2\pi\alpha}\,\tan^{-1}\,(\frac{\alpha}{\beta})^{1/2}+\frac{im^2\omega^2}{32\alpha\beta}\,(\frac{\beta}{\alpha})^{1/2}\,. \tag{A-25}
$$

Since the real part of the right-hand side of Eq. (A-23) is of order unity, we are justified in neglecting the difference between the upper and lower bounds of I_5.

EVALUATION OF THE SPECTRAL DISTRIBUTION FUNCTION

FOR THE IMPURITY SPRING PROBLEM

As indicated in Eq. (17), the spectral distribution function for this problem is given by

$$\bar{g}(\omega) = \frac{4\omega}{\pi} \lim_{\substack{N \to \infty \\ \epsilon \to 0}} \frac{1}{N} \operatorname{Im} \operatorname{Tr} D^{(1)} (\omega^2 + i\epsilon) \; . \tag{A-26}$$

Using Eq. (26) for $D^{(1)}$ and Eq. (36) for $G^{(1)}$, Eq. (A-26) becomes, for small ω^2,

$$\bar{g}(\omega) = \lim_{\substack{N \to \infty \\ \epsilon \to 0}} (4\omega/N\pi) \sum_{\underline{k}} [(4\bar{\alpha}/m)\sin^2(k_x a/2) + (4\bar{\beta}/m)\sin^2(k_y a/2) - \omega^2 - i\epsilon]^{-1}$$

$$= (a^2 \omega/\pi^3) \lim_{\epsilon \to 0} \operatorname{Im} \int_{-\pi/a}^{\pi/a} \int_{-\pi/a}^{\pi/a} [(4\bar{\alpha}/m)\sin^2(k_x a/2) + (4\bar{\beta}/m)\sin^2(k_y a/2) - \omega^2 - i\epsilon]^{-1} dk_x dk_y$$

$$\tag{A-27}$$

Here, $\bar{\alpha}$ and $\bar{\beta}$ are defined by Eqs. (57) and (58), respectively.

Let $I(\omega^2)$ be the integral of Eq. (A-27). It can be written as

$$I = 2(I_1 + I_2) \; , \tag{A-28}$$

where

$$I_1 = \int_{0}^{(2/a)\sin^{-1}(m\omega^2/4\beta)^{1/2}} dk_y$$

$$x \int_{-\pi/a}^{\pi/a} [(4\bar{\alpha}/m)\sin^2(k_x a/2) + (4\bar{\beta}/m)\sin^2(k_y a/2) - \omega^2 - i\epsilon]^{-1} dk_x \; , \tag{A-29}$$

and

$$I_2 = \int_{(2/a)\sin^{-1}(m\omega^2/4\beta)^{1/2}}^{\pi/a} dk_y$$

$$\times \int_{-\pi/a}^{\pi/a} [(4\bar{\alpha}/m)\sin^2(k_x a/2)+(4\bar{\beta}/m)\sin^2(k_y a/2)-\omega^2-i\epsilon]^{-1} \, dk_x \, . \qquad \text{(A-30)}$$

The real part of the denominator of the integrand of I_2 is always positive. As a result, the imaginary part of the integral is of first and higher order in ϵ, and vanishes when the ϵ limit of Eq. (A-27) is taken.

Let

$$\xi^2 = m\omega^2/4\bar{\beta} \, , \qquad \text{(A-31)}$$

$$\omega''^2 = (m/\bar{\alpha}) [\omega^2 - (4\bar{\beta}/m) \sin^2 (k_y a/2)] \, , \qquad \text{(A-32)}$$

$$I_3 = \frac{m}{\bar{\alpha}} \int_{-\pi/a}^{\pi/a} \frac{dk_x}{4 \sin^2(k_x a/2)-\omega''^2-i\epsilon} \, . \qquad \text{(A-33)}$$

Then

$$I_1 = \int_0^{(2/a)\sin^{-1}\xi} I_3 \, dk_y \, . \qquad \text{(A-34)}$$

Substitution of Eq. (A-4) into Eq. (A-33) yields

$$I_3 = \frac{im}{a\bar{\alpha}} \oint \frac{dz}{z^2 - (2 - \omega''^2 - i\epsilon) z + 1} \, , \qquad \text{(A-35)}$$

where the contour is the unit circle.

The denominator of the integrand of Eq. (A-35) is similar to that of Eq. (A-7). It has roots, z_1 and z_2, given by Eqs. (A-9) and (A-10), respectively. As before, z_1 lies inside and z_2 lies outside the unit circle. Thus,

$$I_3 = (mi/a\bar{\alpha})\,[2\pi i/(z_1 - z_2)]$$

$$= (2\pi i/a)\,\{[\omega^2 - (4\bar{\beta}/m)\sin^2(k_y a/2)]$$

$$\times\,[(4\bar{\alpha}/m) + (4\bar{\beta}/m)\sin^2(k_y a/2) - \omega^2]\}^{1/2}\;. \tag{A-36}$$

After some simple manipulations which use Eq. (A-31), substitution of Eq. (A-36) into Eq. (A-34) yields

$$I_1 = \frac{im\pi}{2a(\bar{\alpha}\bar{\beta})^{1/2}}\int_0^{(2/a)\sin^{-1}\xi}\frac{dk_y}{[\xi^2 - \sin^2(k_y a/2)]^{1/2}[1 - (m\omega^2/4\bar{\alpha}) + (\bar{\beta}/\bar{\alpha})\sin^2(k_y a/2)]^{1/2}}\;. \tag{A-37}$$

To lowest order in ω^2, we have

$$I_1 \approx \frac{im\pi}{2a(\bar{\alpha}\bar{\beta})^{1/2}}\int_0^{(2/a)\sin^{-1}\xi}\frac{dk_y}{[\xi^2 - \sin^2(k_y a/2)]^{1/2}}$$

$$= \frac{im\pi^2}{2a^2(\bar{\alpha}\bar{\beta})^{1/2}}\;. \tag{A-38}$$

Substitution of Eqs. (A-28) and (A-38) into Eq. (A-27) yields the density of states

$$\bar{g}(\omega) = \frac{\omega m}{2\pi(\bar{\alpha}\bar{\beta})^{1/2}}\;. \tag{A-39}$$

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FIGURE CAPTIONS

Fig. 1   Pictorial representation of the displacements of atoms in the vicinity of an impurity spring, while taking part in a (10) longitudinal mode. The dashed lines represent the equilibrium positions. The impurity spring, with $\alpha' > \alpha$, is between the atoms denoted 1 and 2. Shear along the lines 3-1-5 and 4-2-6 introduces the factor β into the expression for the effective α.

Fig. 2   Comparison of the effective force constants, $\bar{\alpha}$ and $\bar{\beta}$, as a function of concentration, q, with virtual crystal approximation predictions. Here, $\Delta \alpha / \alpha$ and $\Delta \beta / \beta$ have been taken as -0. 3, while $\alpha / \beta = 9$. The dashed line represents the linear averaging of the force constant, while the solid curve shows the averaging of the inverse of the force constant.
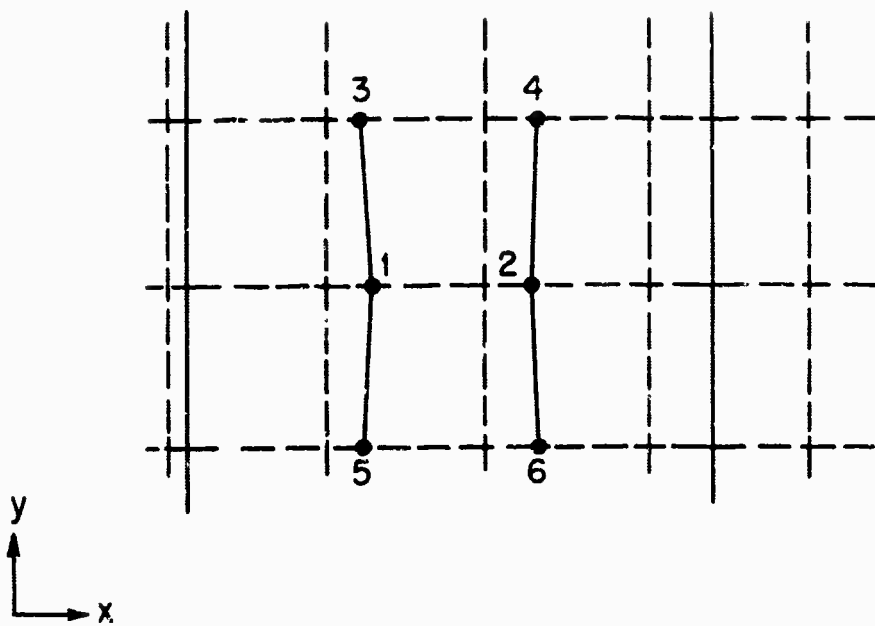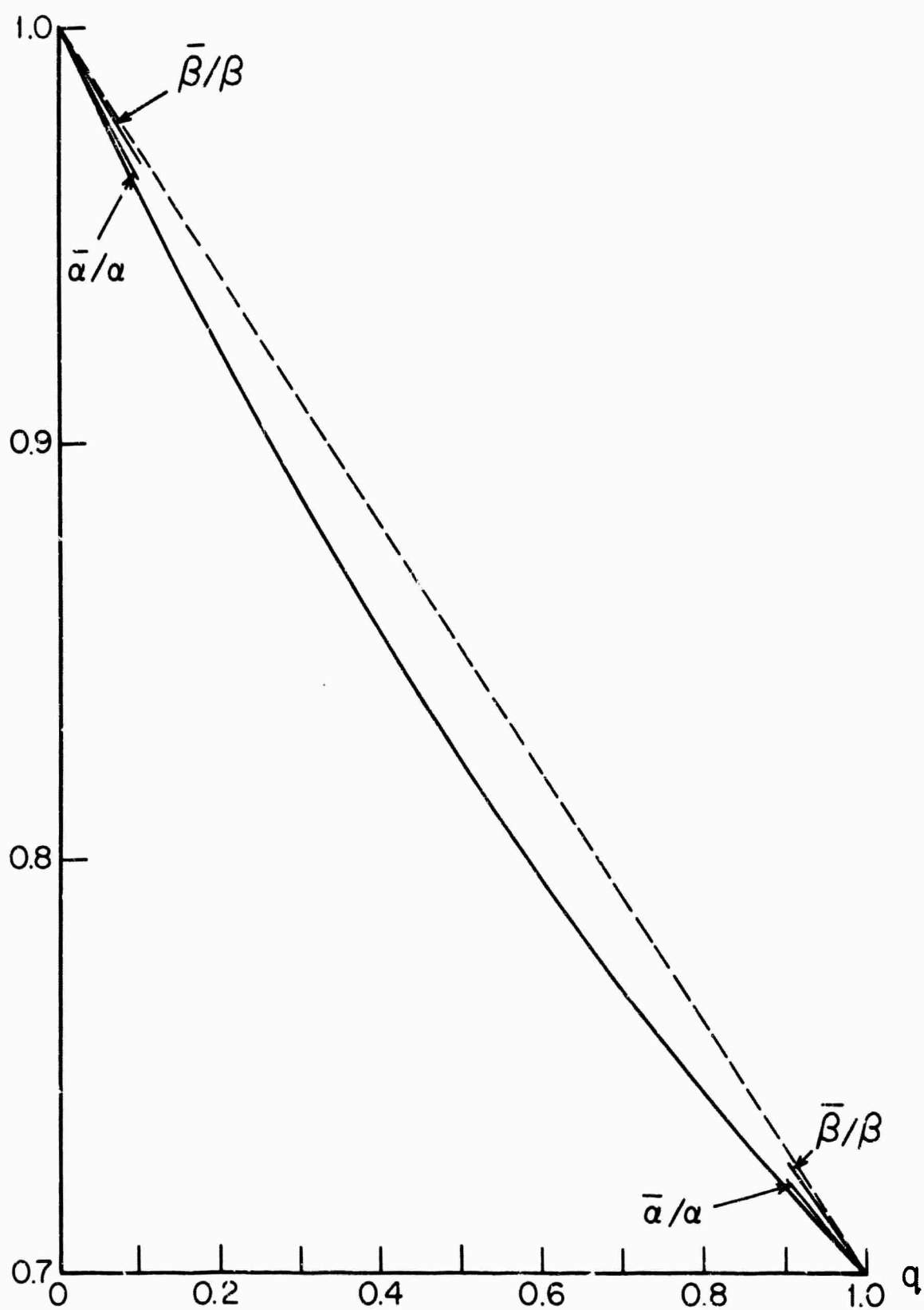
FIGURE   1

FIGURE 2